

**Method Development for Concentration Measurements of SVOCs and
Analysis of Ambient Samples**

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Abstract

Semi-volatile organic compounds (SVOCs) comprise a wide range of toxic pollutants in the atmosphere. Phenols, polycyclic aromatic hydrocarbons (PAHs) and n-alkanes are specific examples of SVOCs that are the focus of this project. SVOCs are compounds with intermediate vapour pressures and can exist in the atmosphere in both gas phase and in particulate matter (PM), which makes their quantification in the atmosphere challenging. Therefore, developing a well-characterized analytical technique for accurate concentration measurement of the selected classes of SVOCs is essential in order to gain more insight into their ambient yield and environmental fate. Recently, a new methodology that allows sampling and analysis of the total (gas phase and PM) concentration of SVOCs in the atmosphere has been developed and tested on a class of SVOCs, namely, nitrophenols (Busca, 2010; Moukhtar et al., 2011; Saccon et al., 2013). This method is based on a sorbent impregnated filter (SIF) technique using conventional high volume air samplers, extraction and analysis by GC-MS.

In this project, the newly developed XAD-4TM SIF was modified, developed and tested to determine its suitability for ambient concentration measurements of other classes of SVOCs like PAHs and n-alkanes. The results of the method validation tests show that the XAD-4TM SIF technique can be used for quantitative measurements of PAHs and n-alkanes in the atmosphere. Atmospheric samples were collected in Toronto as well as in the Alberta Oil Sands region and analyzed using the modified analytical technique. Preliminary results obtained from the Oil Sands samples showed relatively high concentrations for the three classes of SVOCs, particularly in samples impacted by the plume suspected to originate from the Syncrude and/or Suncor mining and upgrading

sites. The carbon preference index (CPI) values obtained for these Oil Sands samples also indicated a substantial anthropogenic impact, even for the samples that were not significantly influenced by nearby emissions from upgrading/refining facilities. The CPI values for some samples were also consistent with some biogenic impact. A comparison of the phase distribution measurements of the three classes of SVOCs demonstrated a systematic dependence between the phase partitioning and vapour pressure for all n-alkanes and most PAHs. However, most of the nitrophenols did not follow this pattern, consistent with findings reported by Facca (2013) and Saccon et al. (2013). Some PAHs with intermediate vapour pressures also did not follow the partitioning expected from their vapour pressure. This indicates that factors other than vapour pressure play a major role in the partitioning of these SVOCs in the atmosphere.

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Common Acronyms Used in This Work

2,6-dime-4-NP	2,6-dimethyl-4-nitrophenol
2-me-3-NP	2-methyl-3-nitrophenol
2-me-5-NP	2-methyl-5-nitrophenol
2-me-4-NP	2-methyl-4-nitrophenol
3-me-4-NP	3-methyl-4-nitrophenol
4-me-2-NP	4-methyl-2-nitrophenol
4-NP	4-nitrophenol
ACE-D ₁₀	Acenaphthene-D ₁₀
ACE-D ₁₀	Acenaphthene-D ₁₀
ACE	Acenaphthene
ACY	Acenaphthylene
ANT	Anthracene
AMS	Air monitoring station
AU	Arbitrary unit
BaA	Benz(a)anthracene
BaP	Benzo(a)pyrene
BbF	Benzo(b)fluoranthene
BkF	Benzo(k)fluoranthene
BghiP	Benzo(g,h,i)perylene
BSTFA	N,O-bis(trimethylsilyl) trifluoroacetamide
C ₁₃	Tridecane
C ₁₄	Tetradecane
C ₁₅	Pentadecane
C ₁₆	Hexadecane
C ₁₇	Heptadecane
C ₁₈	Octadecane
C ₁₉	Nonadecane

C ₂₀	Eicosane
C ₂₁	Heneicosane
C ₂₂	Docosane
C ₂₃	Tricosane
C ₂₄	Tetracosane
C ₂₅	Pentacosane
C ₁₂ D ₂₆	Dodecane-D ₂₆
C ₁₉ D ₄₀	Nonadecane-D ₄₀
C _T	Target compound concentration
Cal _{IS}	Internal standard response factor from calibration curve
Cal _T	Target compound response factor from calibration curve
CPI	Carbon preference index
CRY	Chrysene
CRY-D ₁₂	Chrysene-D ₁₂
dBahA	Dibenz(a,h)anthracene
DL	Detection limit
f _{om}	Weight fraction absorbing in organic matter
FLT	Fluoranthene
FLU	Fluorene
GC-MS	Gas chromatography mass spectrometry
GFF	Glass fiber filter
HMB	Hexamethylbenzene
HPLC	High performance liquid chromatography
IND	Indeno(1,2,3-cd)pyrene
IS	Internal Standard
K _p	Partitioning coefficient
m _T	Mass of target compound
MM	Molecular mass

NA	Not available
NAP	Naphthalene
P _A	Peak area
P _L [°]	Sub-cooled liquid vapour pressure
PAH	Poly aromatic hydrocarbon
PHE	Phenanthrene
PHE-D ₁₀	Phenanthrene-D ₁₀
PM	Particulate matter
PUF	Polyurethane foam
PYR	Pyrene
Q _l	Enthalpy for desorption from surface
Q _v	Enthalpy of vaporization of the sub-cooled liquid
R	Gas constant 8.314 J K ⁻¹ mol ⁻¹
QFF	Quartz fiber filter
SIF	Sorbent impregnated filter
SIM	Selective ion mode
SPE	Solid phase extraction
SVOC	Semi-volatile organic compounds
TIC	Thin layer chromatography
TSP	Total suspended particulate matter
V	Sampling volume
VOC	Volatile organic compound
ζ	Activity coefficient

1 Introduction

Many organic compounds found in the atmosphere are classified as semi-volatile organic compounds (SVOCs). As proposed by Junge (1977), SVOCs are compounds with vapour pressures that fall within the range of 10^{-6} to 10^{-2} Pa. Owing to their intermediate vapour pressures in the atmosphere, SVOCs tend to partition between the gas phase and PM in amounts that depend on such factors as temperature, aerosol composition and relative humidity in the atmosphere. Knowledge of the relative contribution from both gas phase and PM is important in order to fully understand the formation and processing of SVOCs in the atmosphere (Bidleman, 1988).

Phenols, polycyclic aromatic hydrocarbons (PAHs) and n-alkanes are three important classes of SVOCs in the atmosphere that are studied in this project. These three classes of SVOCs are being analyzed for two main reasons. One is that they cover a wide range of physical-chemical properties that offer more information about the gas-particle phase distribution of these SVOCs in the atmosphere. Second, in recent years there has been concern that a growing amount of these organic pollutants are emitted into the atmosphere due to increasing industrial development in the Alberta Oil Sands region. Despite their potentially harmful qualities, there are few detailed studies of the organic pollutants emitted from Alberta Oil Sands mining and related activities in peer-reviewed literature (Kelly et al., 2009; Simpson et al., 2010; Galarnau et al., 2014; Parajulee and Wania, 2014).

The gas-particle partitioning characteristic of SVOCs makes their quantification in the atmosphere challenging. In order to gain a better understanding of the atmospheric yield of these pollutants, it is critical to develop a well-characterized technique that

allows for the measurement of the total (gas phase and PM) ambient concentrations of SVOCs. Recently, a new methodology has been developed that allows for the sampling and analysis of the total (gas phase and PM) concentration of nitrophenols, in the atmosphere (Busca, 2010; Moukhtar et al., 2011; Saccon et al., 2013). This method is based on a sorbent impregnated filter (SIF) technique that uses conventional high volume air sampling. More specifically, for this method, two filters—one uncoated quartz fiber filter (QFF) (for PM collection) and one SIF coated with XAD-4TM adsorbent (for gas phase and PM collection)—were used in series or in parallel to obtain information on phase partitioning of SVOC.

Recent studies in Dr. Rudolph's research group employing the newly developed SIF method showed that, for several phenols, the distribution between gas phase and PM does not follow the dependence expected from their vapour pressures. Also, research performed by Saccon (2013) reported that the atmospheric yields of these phenols were orders of magnitude lower than predicted by some laboratory studies (Forstner et al., 1997; Irei, 2008). To better understand some of these gaps in our knowledge, the thought was to apply the XAD-4TM SIF method for atmospheric concentration measurements of other classes of SVOCs, namely, PAHs and n-alkanes. Aside from the adverse health effects of PAHs and n-alkanes on humans, they were selected since their chemical and physical properties are better known compared to nitrophenols.

High volume QFF sampling is a well-established technique for ambient concentration measurements of SVOCs like PAH and n-alkanes. However, QFF only collects PM with some possible gas phase artifacts. XAD-4TM is a resin that has been previously used on denuders, low volume filters, and polyurethane foam (PUF) plugs as a

SVOC and VOC adsorbent (Gundel and Lane, 1999; Eiguren-Fernandez et al., 2004; Possanzini et al., 2004; Mugica et al., 2010). Only one study by Galarneau et al. (2006), used XAD-4TM SIF for quantitative ambient concentration measurements of a few PAH compounds in both the gas phase and PM.

Although a denuder, which is able to separate the gas phase from the particle phase based on diffusion characteristics, would be the best method to sample the gas phase and PM SVOCs in the atmosphere, there are several advantages associated with using high-volume filters as opposed to the denuder-filter pack. Firstly, obtaining samples and analyzing them is much less demanding using the high volume method, especially for measurements at remote locations where logistic support is limited. Secondly, due to the much larger air volumes sampled, the impact of blank values will be reduced and the detection limits as well as the precision of the analysis will be improved. Finally, it has been shown recently that the use of high volume filter sampling for SVOCs allows isotope ratio measurement of these compounds at atmospheric concentrations below 1 ng m⁻³ (Saccon et al., 2013). While obtaining isotope ratio measurements is not the primary objective of this research, a methodology that allows sampling that is suitable for the future analysis of gas-chromatography coupled with online isotope ratio mass spectrometry (GC-IRMS) would be valuable due to the new insights that such an analysis can provide (Rudolph et al., 2002; Goldstein and Shaw, 2003; Gensch et al., 2014).

The principal goal of this project was to modify, develop and validate a method for the quantitative analysis of ambient PAHs and n-alkanes using XAD-4TM SIFs. Ambient sampling was done in both Toronto and in the Alberta Oil Sands region. Results from these two locations were used to gain a better understanding of both the presence and

magnitude of the selected classes of SVOCs. This information was also used to study the phase distribution of these compounds and comparison between the two locations gave insight into similarities and differences in sources.

Background information on gas-particle partitioning, Oil Sands mining and a description of the various methods used by other studies for ambient measurements of the selected classes of SVOCs are provided in chapter 2. The experimental procedure, including the filter preparation, sampling, sample extraction and analysis procedure are outlined in chapter 3. Chapter 4 presents the results obtained from the method validation tests as well as results from ambient samples; the results are discussed in chapter 5. The conclusions as well as suggestions for future work are provided in chapter 6.

2 Theory and Background

This section begins with a brief description of the characteristics and sources of the selected classes of SVOCs. This is followed by a brief overview of the ambient measurements of PAHs, n-alkanes, and nitrophenols reported in the literature. Moreover, the Oil Sands mining and the potential pollutants expected from the Oil Sands developments are briefly discussed.

2.1 PAHs

PAHs are organic substances comprised of two or more fused aromatic rings and are found in the gas phase or adsorbed onto airborne PM. Generally, PAHs with three or four rings are found in both gas phase and PM due to their intermediate vapour pressures but those that contain more than four rings are mainly found in PM in the atmosphere (Yamasaki et al., 1982; Halsall et al., 1994; Keyte et al., 2013). There are hundreds of individual PAHs present in the environment but only the 16 that are classified as priority pollutants by the US Environmental Protection Agency (US EPA, 1998) are the focus of this study. The 16 PAH compounds along with their vapour pressures are summarized in Table 2.1.

Table 2.1: Vapour pressures of target PAHs in the atmosphere (Mackay et al., 1992; Shiu and Ma, 2000).

Compound	Molecular Formula	Number of Rings	Molecular Mass (g mol ⁻¹)	Vapour Pressure (Pa) at 298 K
Naphthalene	C ₁₀ H ₈	2	128.17	1.1 × 10 ¹
Acenaphthylene	C ₁₂ H ₈	3	152.19	9 × 10 ⁻¹
Acenaphthene	C ₁₂ H ₁₀	3	154.21	2.9 × 10 ⁻¹
Fluorene	C ₁₃ H ₁₀	3	166.22	9.0 × 10 ⁻²
Phenanthrene	C ₁₄ H ₁₀	3	178.23	1.8 × 10 ⁻²
Anthracene	C ₁₄ H ₁₀	3	178.23	1.1 × 10 ⁻³
Fluoranthene	C ₁₆ H ₁₀	4	202.25	1.2 × 10 ⁻³
Pyrene	C ₁₆ H ₁₀	4	202.25	6.0 × 10 ⁻⁴
Benz(a)anthracene	C ₁₈ H ₁₂	4	228.29	2.8 × 10 ⁻⁵
Chrysene	C ₁₈ H ₁₂	4	228.29	5.7 × 10 ⁻⁷
Benzo(a)pyrene	C ₂₀ H ₁₂	5	252.31	7.0 × 10 ⁻⁷
Benzo(b)fluoranthene	C ₂₀ H ₁₂	5	252.31	5.0 × 10 ⁻⁷
Benzo(k)fluoranthene	C ₂₀ H ₁₂	5	252.31	5.2 × 10 ⁻⁸
Indeno(1,2,3-cd)pyrene	C ₂₂ H ₁₂	6	276.33	1.3 × 10 ⁻⁸
Benzo(g,h,i)perylene	C ₂₂ H ₁₂	6	276.33	1.0 × 10 ⁻⁸
Dibenz(a,h)anthracene	C ₂₂ H ₁₄	6	278.35	3.7 × 10 ⁻¹⁰

PAHs are products of incomplete combustion and other than being emitted from forest fires, they are predominantly emitted from anthropogenic sources such as fossil fuel combustion, oil refining, power plants, domestic heating and diesel powered vehicles (Masclat et al., 1986; Rogge et al., 1993; Harrison et al., 1996; Yang et al., 1998).

2.2 n-Alkanes

n-Alkanes are another important group of organic compounds in atmospheric aerosols that are also found in both the gas phase and PM at ambient temperature. These compounds are non-polar and rather stable in chemical behaviour. The vapour pressures of the target n-alkanes studied in this project are summarized in Table 2.2.

Table 2.2: Vapour pressures of target n-alkanes in the atmosphere (Ruzicka and Majer 1993).

Compound	Molecular Formula	Molecular Mass (g mol ⁻¹)	Vapour Pressure (Pa) at 298 K
Tridecane	C ₁₃ H ₂₈	184	0.57 × 10 ¹
Tetradecane	C ₁₄ H ₃₀	198	0.18 × 10 ¹
Pentadecane	C ₁₅ H ₃₂	212	5.76 × 10 ⁻¹
Hexadecane	C ₁₆ H ₃₄	226	1.91 × 10 ⁻¹
Heptadecane	C ₁₇ H ₃₆	240	6.15 × 10 ⁻²
Octadecane	C ₁₈ H ₃₈	254	2.01 × 10 ⁻²
Nonadecane	C ₁₉ H ₄₀	268	6.57 × 10 ⁻³
Eicosane	C ₂₀ H ₄₂	282	2.09 × 10 ⁻³
Heneicosane	C ₂₁ H ₄₄	296	6.39 × 10 ⁻⁵
Docosane	C ₂₂ H ₄₆	310	1.01 × 10 ⁻⁵
Tricosane	C ₂₃ H ₄₈	324	1.61 × 10 ⁻⁶
Tetracosane	C ₂₄ H ₅₀	338	1.60 × 10 ⁻⁷
Pentacosane	C ₂₅ H ₅₂	352	3.20 × 10 ⁻⁸

Unlike PAHs, n-alkanes are emitted from both anthropogenic and biogenic sources. Anthropogenic sources of n-alkanes include fossil fuel combustion, lubricant oils and biomass burning, while wind erosion of epicuticular waxes from vascular plants, direct suspension of pollen and vegetation debris are major biogenic sources of n-alkanes

(Simoneit et al., 1977; Rogge et al., 1993a; Rogge et al., 1993c; Bi et al., 2003). In order to identify the origin of organic aerosols, the carbon preference index (CPI) can be used. CPI is the ratio of the concentration of odd over even carbon number of n-alkanes, giving a measure of the degree of biogenic over anthropogenic sources (Eichmann et al., 1979). In particular, anthropogenic emissions from fossil fuels generate a random distribution of odd versus even carbon number yielding a low CPI value of 1 to 3 (Eichmann et al., 1979; Mazurek et al., 1989) whereas hydrocarbons originating from biogenic source exhibit a strong odd carbon number predominance showing a high CPI value of 3 to 30 (Eichmann et al., 1979; Mazurek et al., 1989; Simoneit et al., 1989). As such, unique n-alkane distribution patterns are obtained for anthropogenic (Figure 2.1a) and biogenic (Figure 2.1b) sources, which may be used to identify the origin of the atmospheric aerosols (Rogge et al., 1993a; Kadowaki, 1994).

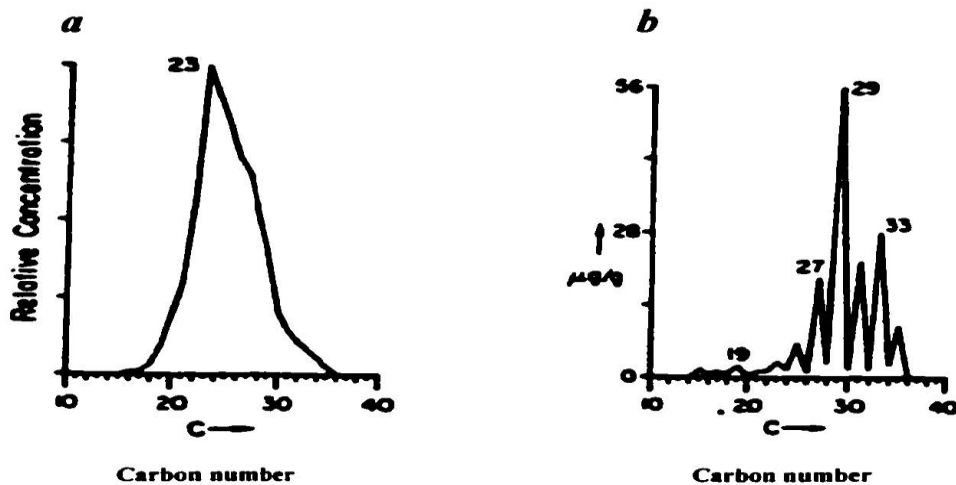


Figure 2.1: n-Alkane carbon distribution patterns: (a) auto engine exhaust, with no odd even preference (b) composited vegetation, showing a saw-tooth pattern with an odd n-alkane preference (Simoneit et al., 1984).

2.3 Nitrophenols

Unlike PAHs and n-alkanes, nitrophenols are secondary pollutants since they are predominantly formed in the atmosphere from the photo-oxidation of aromatic volatile organic compounds (VOCs) such as toluene, benzene and m-xylene, which are mainly emitted from anthropogenic sources (Forstner et al., 1997; Atkinson, 2000; Jang and Kamens, 2001; Moukhtar et al., 2011; Saccon et al., 2013). However, primary emission sources have been reported in the literature for some of the nitrophenols studied in this project (Nojima et al., 1983; Tremp et al., 1993; Inomata et al., 2013, 2015). The target nitrophenols and their vapour pressures are shown in Table 2.3.

Table 2.3: Vapour pressures of target nitrophenols in the atmosphere (Gong, X; private communication).

Compound	Vapour Pressure (Pa) at 303 K
4-methyl-2-nitrophenol	1.11×10^1
4-nitrophenol	1.03×10^{-2}
3-methyl-4-nitrophenol	3.13×10^{-3}
2-methyl-4-nitrophenol	8.69×10^{-3}
2,6-dimethyl-4-nitrophenol	6.42×10^{-4}

2.3.1 Formation Mechanism of Nitrophenols

Methyl-nitrophenols have been found to be the products of reaction of toluene with the hydroxyl radical (HO) (Atkinson et al., 1994; Forstner et al., 1997). This reaction, shown in Figure 2.2, is initiated by either HO radical addition to the benzene ring or by H-atom abstraction from the methyl group. The H-atom abstraction has been found to be a minor pathway since it accounts for ≤ 10 % of the overall reaction (Atkinson et al.,

1994). Therefore a more efficient reaction is achieved by the HO radical addition to the aromatic ring in any of the ortho-, para-, or meta- positions, with the ortho- position thermodynamically favoured (Andino et al., 1996). The methyl hydroxycyclohexadienyl radical formed from the HO radical addition pathway, subsequently react with atmospheric oxidants such as oxygen (O_2) and nitrogen dioxide (NO_2) to form methyl phenols (cresols) (Atkinson et al., 1994). The cresols can then react with HO radical and subsequently undergo nitration by reacting with NO_2 in the atmosphere to form methyl-nitrophenols. As such, the main products from this reaction are expected to be 2-methyl-4-nitrophenol, 3-methyl-4-nitrophenol and 4-methyl-2-nitrophenol.

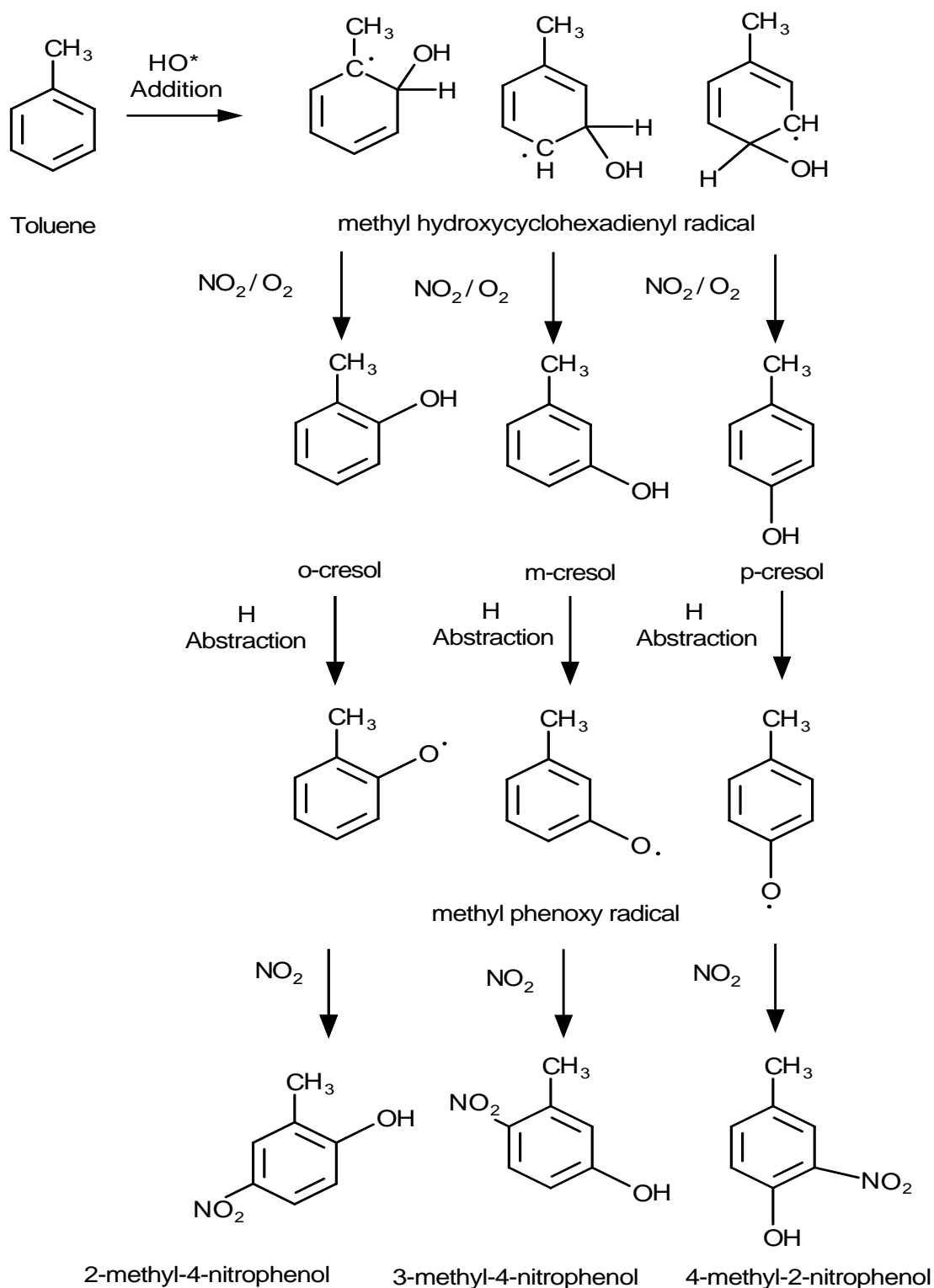


Figure 2.2: Reaction mechanism for formation of methyl-nitrophenols from toluene (adapted from Forstner et al., 1997).

2,6-dimethyl-4-nitrophenol is proposed to be formed from the photo-oxidation of m-xylene and is expected to follow the same reaction pathway as the oxidation of toluene by the HO radical, which is shown in Figure 2.3 (Zhao et al., 2005).

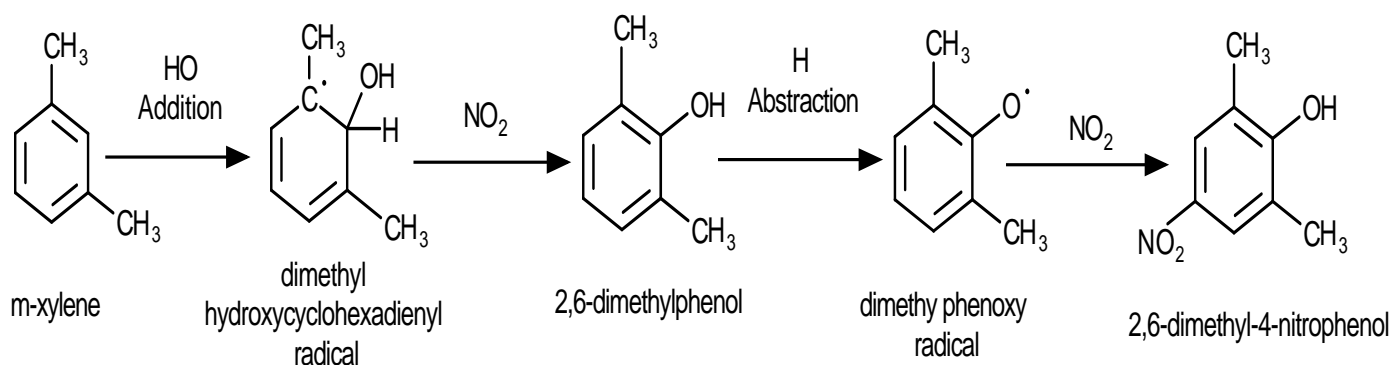


Figure 2.3: Formation mechanism of 2,6-dimethyl-4-nitrophenol from m-xylene (adapted from Zhao et al., 2005)

The formation mechanism of 4-nitrophenol, adapted from Atkinson et al. (1992) is shown in Figure 2.4. This compound is formed from photo-oxidation of phenol, which is emitted from anthropogenic sources or formed through photo-oxidation of benzene. According to the mechanism proposed by Atkinson et al. (1992), phenol undergoes H-atom abstraction from the aromatic ring followed by reaction with NO_2 to form 4-nitrophenol. An alternative formation mechanism was proposed by Bolzacchini et al. (2001) which involves an addition of nitrate (NO_3) to the phenolic carbon, followed by NO_2 addition to the para- carbon and a final loss of nitric acid to form 4-nitrophenol. However, due to the rapid photolysis of NO_3 during the day, this reaction is limited to nighttime chemistry.

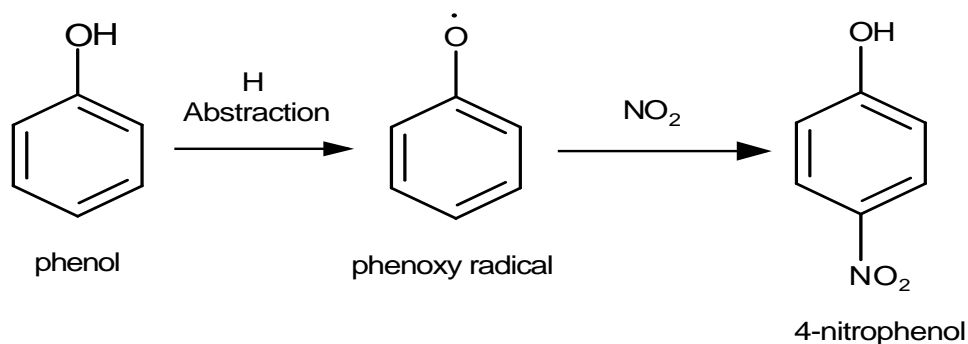


Figure 2.4: Formation mechanism of 4-nitrophenol from phenol (adapted from Atkinson et al., 1992).

2.4 Gas Phase and PM Partitioning

The target SVOCs selected for this study fall within the semi-volatile range on account of their respective vapour pressures (Tables 2.1, 2.2, and 2.3) and can partition between the gas phase and PM in the atmosphere. Figure 2.5 presents the PM percentage as a function of vapour pressure for the selected classes of SVOCs obtained from different studies. The results show that except for nitrophenols, most n-alkanes and PAHs follow the phase partitioning expected from their vapour pressures. It should be noted that there are some limitations associated with the direct comparison of the phase distribution of SVOCs from different studies. For example, the PM concentration and composition as well as sampling conditions can vary significantly between different sampling locations. Furthermore, the sampling and analysis procedures used by different studies are also important parameters that can impact the comparison between the observed phase distributions of SVOCs from different sites. The impact from these factors can be eliminated if the phase distribution measurements for different classes of SVOCs are obtained from the same sampling event using the same sampling and analysis technique.

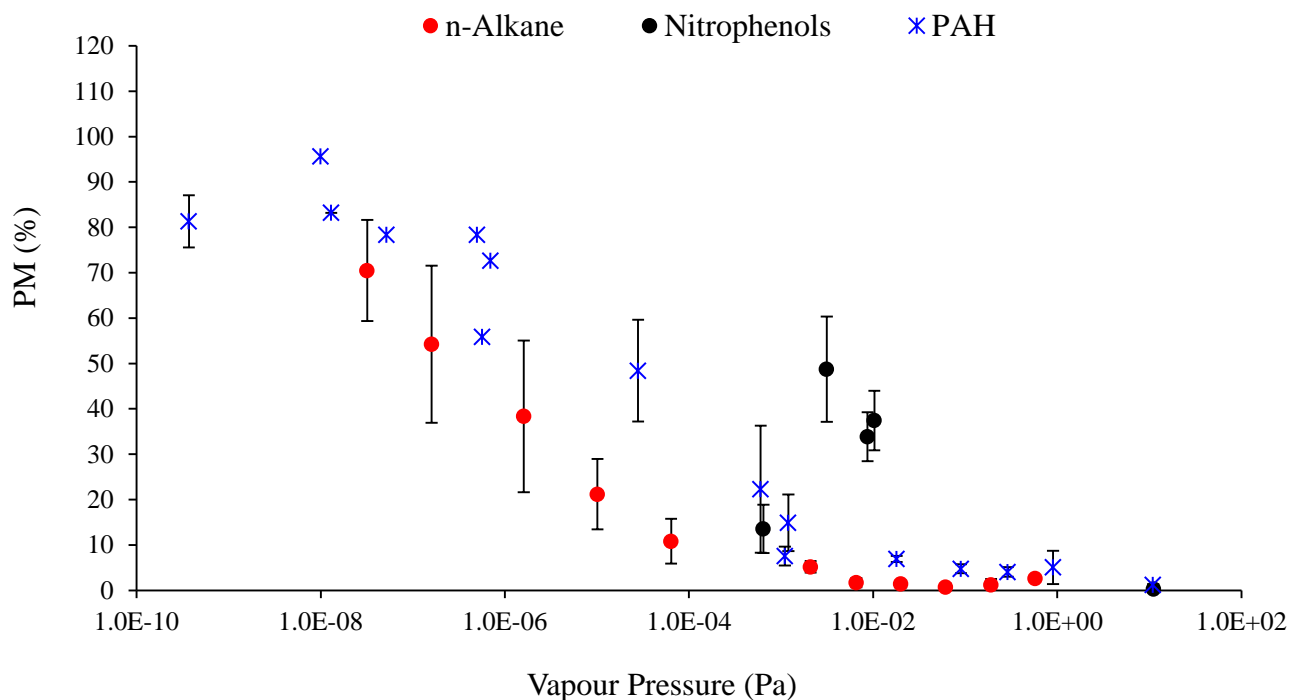


Figure 2.5: Average PM percentage of individual PAHs (Mandalakis et al., 2002; Park et al., 2002; Possanzini et al., 2004) n-alkanes (Leal-Granadillo et al., 2000; Mandalakis et al., 2002; Cincinelli et al., 2007) and nitrophenols (Facca, 2013) plotted against vapour pressure. The error bars represent the error of the mean.

The partitioning of SVOCs between the gas phase and PM is described as either surface adsorption on the particle or absorption into organic matter depending on the nature of the particle (i.e. solid or liquid) (Junge, 1977; Pankow, 1987; Pankow, 1994). In general, the partitioning of SVOCs between gas phase and PM has been parameterized by the partitioning constant, K_p in $\text{m}^3 \mu\text{g}^{-1}$ in accordance with the following equation (Pankow, 1987):

$$K_p = \frac{C_p / C_{TSP}}{C_g} \quad \text{Eq. 2.1}$$

Here, C_p and C_g are the organic compound concentrations in the PM and gas phase, respectively; and C_{TSP} is the concentration of total suspended particulate matter (TSP) in

$\mu\text{g m}^{-3}$. If the partitioning is dominated by simple physical adsorption, the partitioning coefficient, K_p , is calculated using Eq. 2.2 (Pankow, 1987).

$$K_p = \frac{N_s a_{TSP} T e^{(Q_l - Q_v)/RT}}{1600 P_L^\circ} \quad \text{Eq. 2.2}$$

Here, N_s is the surface area concentration of adsorption sites in mol cm^{-2} , a_{TSP} is the specific surface area of the TSP in $\text{cm}^2 \text{g}^{-1}$, T is the temperature in K, R is the gas constant ($8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{mol}^{-1}$), and P_L° is the sub-cooled liquid vapour pressure in torr. Q_l is the enthalpy for desorption from the surface and Q_v is the enthalpy for volatilization of sub-cooled liquid in kJ mol^{-1} . Pankow also showed that if the partitioning is dominated by absorption, the partitioning coefficient, K_p , is calculated using Eq. 2.3 (Pankow, 1994).

$$K_p = \frac{f_{om} 760 RT}{MM_{om} \zeta P_L^\circ 10^6} \quad \text{Eq. 2.3}$$

Here, f_{om} is the fraction of organic matter on the TSP and MM_{om} is the molecular mass of the organic matter. ζ is the activity coefficient of the absorbate in the organic matter.

2.5 Ambient Sampling of SVOCs

Sampling ambient air onto glass or quartz fiber filters using a high volume air sampler is a common technique used to collect PM from ambient air (Finlayson-Pitts and Pitts, 2000). In order to enable the collection of both gas phase and PM SVOC, a filter is typically followed by one or more gas traps such as PUF, organic resins – Tenax, XAD

and Chromosorb, or combination of both PUF and organic resins. Another technique that allows collection of the total (gas phase and PM) concentration of SVOC is the SIF technique, where XAD or similar organic resins are used as sorbents. XAD is a trade name used for styrene-divinylbenzene copolymer resins, which are non-polar, hydrophobic, and porous adsorbents. Although there are a wide variety of XAD adsorbents available, XAD-4TM resin was selected by Busca (2010) because of its higher surface area compared to the other XAD resins. One of the main advantages of using the SIF technique as opposed to other technique mentioned above is that the total (gas phase and PM) concentrations of SVOCs can be measured from only one extracted filter. This significantly reduces the time, material and errors associated with separate extractions.

2.6 Ambient Measurements of PAHs, n-Alkanes and Nitrophenols

Atmospheric levels of PAHs and n-alkanes have been widely measured around the world and a large amount of data is available regarding their concentrations as well as their phase distributions in the atmosphere. From these studies, only a limited numbers were selected in this work for PAHs (Halsall et al., 1994; Cotham and Bidleman, 1995; Odabasi et al., 1999; Mandalakis et al., 2002; Park et al., 2002; Possanzini et al., 2004; Demircioglu et al., 2011) and n-alkanes (Leal-Granadillo et al., 2000; Mandalakis et al., 2002; Bi et al., 2003; Cincinelli et al., 2007) in order to provide some information about the range of ambient PAHs and n-alkanes concentrations reported. The results from these studies are summarized in Tables 2.4 and 2.5 for n-alkanes and PAHs, respectively. Halsall et al. (1994) measured ambient concentrations of the total (gas phase and PM) PAHs at an urban site in London, UK using a high volume air sampler equipped with a

glass fiber filter (GFF) to collect PM followed by two PUF plugs connected in series to collect gas phase compounds. Cotham and Bidleman (1995) collected ambient samples at a rural site in Green Bay, USA in February 1998 by drawing air through a GFF to collect PM and then through a PUF plug to collect gas phase PAHs. Odabasi et al. (1999) used GFF to collect PM and a modified cartridge containing XAD-2TM resin placed between layers of PUF plugs to collect gas phase PAHs at an urban area in Chicago. Mandalakis et al. (2002) reported ambient concentrations of both PAHs and n-alkanes resulting from analysis of samples collected at an urban area in Athens, Greece. They used a similar sampling approach as the one used by Halsall et al. (1994). A high volume PUF air sampler was employed by Park et al. (2002) in order to sample PAHs at an urban site in Seoul, Korea. PM and Gas phase PAHs were collected on QFF and PUF, respectively. Possanzini et al. (2004) used QFFs and XAD-4TM coated annular denuders to sample PM and Gas phase PAHs, separately. Demircioglu et al. (2011) measured both PM and gas phase PAHs in an urban and a suburban site in Izmir, Turkey using a similar sampling approach as the one used by Odabasi et al. (1999). Gas phase and PM concentrations of n-alkanes were measured in Oviedo, Spain by Leal-Granadillo et al. (2000) using a sampling method similar to the one used by Halsall et al. (1994). Cincinelli et al. (2007) also used this sampling method for gas phase and PM measurements of n-alkanes in an industrial area in Prato, Italy. Bi et al. (2003) sampled total (gas phase and PM) concentrations of n-alkanes in urban area of Guangzhou, China using a high volume air sampler equipped with GFF for PM collection and a one-and-a-half PUF plug connected in series to collect gas phase compounds.

Table 2.4: Atmospheric concentrations of target n-alkanes reported in literature.

Compound	Concentration (ng m ⁻³)						
	Leal-Granadillo et al. (2000)		Mandalakis et al. (2002)		Bi et al. (2003)	Cincinelli et al. (2007)	
	Gas	PM	Gas	PM	Gas +PM	Gas	PM
Tridecane					3.26		
Tetradecane			0.83	ND	3.03		
Pentadecane	ND	ND	1.83	0.10	2.53	3	ND
Hexadecane	1	ND	3.89	0.15	3.31	8	ND
Heptadecane	9	ND	4.00	0.09	2.91	15	ND
Octadecane	24	ND	5.07	0.10	4.07	22	0.5
Nonadecane	16	ND	5.20	0.19	5.67	30	0.5
Eicosane	9	0.5	3.92	0.31	7.98	33	1
Heneicosane	4	1	5.05	0.52	13.16	31	1
Docosane	3.5	2	3.86	0.76	16.73	25	3
Tricosane	1	2.5	3.97	1.41	15.78	19	4
Tetracosane	0.5	4	2.70	1.50	11.03	13	8
Pentacosane	0.5	6	2.17	2.71	10.69	8	14

ND: not detected.

Table 2.5: Atmospheric concentrations of target PAHs reported in literature.

Compound	Concentration (ng m ⁻³)										
	Halsall et al. (1994)	Cotham and Bidlema (1995)	Odabasi et al. (1999)	Mandalakis et al. (2002)		Park et al. (2002)		Possanzini et al. (2004)		Demircioglu et al. (2011)	
	Gas + PM	Gas + PM	Gas +PM	Gas	PM	Gas	PM	Gas	PM	Gas	PM
NAP						11.09	0.14	687	12		
ACY						7.26	0.12	39	4.6		
ACE	2.1		76.9			3.14	0.21	57	2.2		
FLU	13.4	3.3	74.8	1.28	0.10	6.20	0.26	18	0.9	^a 4.1, ^b 12.5	^a 0.6, ^b 0.1
PHE	76.1	6.7	200.3	6.08	0.46	15.03	1.46	71	7.2	^a 11.7, ^b 40.8	^a 1.9, ^b 1.0
ANT	5.0	0.06	14.1	0.89	0.14	2.52	0.18	5.6	0.5	^a 0.5, ^b 5.6	^a 0.1, ^b 0.1
FLT	7.4	1.4	44.1	2.79	0.19	5.83	2.27	18	3.5	^a 3.7, ^b 27.3	^a 1.5, ^b 2.8
PYR	6.8	0.6	24.6	1.91	0.19	10.31	2.25	7.6	9.2	^a 2.4, ^b 20.2	^a 1.4, ^b 3.1
BaA	0.8	0.14	2.1	0.16	0.11	0.80	1.82	0.4	1.4	^a 0.1, ^b 0.6	^a 0.5, ^b 3.0
CRY	1.5	0.35	3.6			0.84	2.78	0.5	3.9	^a 0.4, ^b 1.6	^a 1.5, ^b 6.2
BbF	1.1	0.47	2.3				4.89	0.7	6.8	^a 0.05, ^b 0.03	^a 0.9, ^b 3.4
BkF	1.0	0.47	1.9				4.89	0.7	6.8	^a 0.02, ^b 0.02	0.8, 3.6
BaP	0.6	0.12	1.6				2.55	0.3	2.4	^a 0.02, ^b 0.008	^a 0.7, ^b 3.1
IND		0.12	1.2	ND	0.45		3.59	ND	1.6	^a 0.01, ^b 0.006	^a 0.9, ^b 3.4
dBahA				ND	0.08		0.55			^a 0.02, ^b 0.003	^a 0.4, ^b 1.3
BghiP	4.4	0.18	1.1	ND	0.44		3.21	0.5	2.4	^a 0.03, ^b 0.008	^a 0.9, ^b 3.4

ND: not detected

^a suburban site

^b urban site.

Ambient measurements of nitrophenols, on the other hand, have been studied by a limited number of research groups (Herterich and Hermann, 1990; Nishioka and Lewtas, 1992; Morville et al., 2004; Cecinato et al., 2005; Moukhtar et al., 2011; Saccon et al., 2013) and are shown in Table 2.6. Herterich and Herrmann (1990) measured ambient concentration of nitrophenols for the first time at two German hill sites by drawing air through a column filled with XAD-2TM adsorbent. Nishioka and Lewtas (1992) collected samples in Boise, Idaho using a PM₁₀ sampler with a Teflon glass filter for PM collection and 200 g of XAD-2TM resin to collect gas phase nitrophenols. Cecinato et al. (2005) reported ambient measurements of gas phase and PM nitrophenols in Rome, Italy. They used a KOH coated denuder and Teflon fiber filters to collect gas phase and PM nitrophenols, separately. Morville et al. (2004) measured gas phase and PM concentrations of nitrophenols in Strasbourg, France using a high volume air sampler equipped with GFF and 20 g of XAD-2TM resins. Ambient concentrations of nitrophenols were also measured at York University, Toronto by Saccon et al. (2013) using a high volume air sampler equipped with XAD-4TM SIF to collect total (gas phase and PM) concentrations of nitrophenols.

Table 2.6: Atmospheric concentrations of target nitrophenols reported in literature.

Compound	Concentration (ng m ⁻³)						
	Herterich and Hermann (1990)	Nishioka and Lewtas, (1992)		Morville, et al. (2004)	Cecinato et al. (2005)		Saccon et al. (2013)
	Gas	Gas	PM	Gas + PM	Gas	PM	Gas + PM
4-methyl-2-nitrophenol	10.7-26.0	1.8	ND	0.58	6.9	2.9	2.78
4-nitrophenol	2.1-5.6	0.85	2.7		3.9	18	6.88
3-methyl-4-nitrophenol		0.54	0.77	0.69	2.2	7.8	1.09
2-methyl-4-nitrophenol		2.7	1.2				3.22
2,6-dimethyl-4-nitrophenol					2.0	5.9	1.06

ND: not detected

Atmospheric measurements of PAHs, n-alkanes and nitrophenols reported by each research group (Tables 2.4, 2.5 and 2.6) vary considerably due to the fact that they are acquired in different regions using a variety of sampling and analysis techniques.

2.7 SVOC Emissions from Oil Sands Mining

The Athabasca Oil Sands region in the northern Alberta, Canada is the third largest oil deposit in the world (Alberta energy, c1995-2015). The Oil Sands consist of a mixture of sand (83 % to 85 %), water (4 % to 6%), and bitumen (10 % to 12%), which is a heavy and viscous form of petroleum (Yang et al. 2011). The hydrocarbon content of Oil Sands bitumen is estimated to be between 35 % and 45 % (Strausz and Lown, 2003; Yang et al., 2011). Currently, surface mining is the most common method used for Oil Sands recovery. Once mined, bitumen is extracted from Oil Sands using a hot water extraction process. The water and sands are removed from the extracted bitumen using a solvent/diluent such as naphtha, which is made up of mixtures of aliphatic hydrocarbons, C₃ to C₁₄, as well as aromatic compounds such as benzene, toluene, ethyl-benzene, and xylenes (Siddique et al., 2006). The contaminated water used for the extraction process is then transferred to large storage areas called tailing-ponds. Following the extraction, the bitumen is upgraded using heat, pressure and catalysts in order to produce synthetic crude oil.

The mining facilities in the Alberta Oil Sands region are located in the center of a forested area that lacks a large population and other industrial facilities. Therefore, emissions from these facilities are more obvious against the relatively clean background. Based on a study by Simpson et al. (2010), large quantities of organic pollutants can

potentially be emitted from Oil Sands upgrading activities as well as direct emissions from solvents/diluents used for bitumen extraction. According to the findings reported by Simpson et al. (2010), mixing ratios of a number of aromatic VOCs showed significant enhancement over the local background in the Oil Sands region. Toluene was reported as the most abundant aromatic followed by xylenes and benzene. Recent studies by Galarneau et al. (2014) and Parajulee and Wania (2014) have also suggested that tailing-ponds may be a significant contributor to PAH emission in this region. Other sources of organic pollutants in this region include emissions from off-road heavy hauler mine fleets, which are used for Oil Sands operations (Watson et al., 2013), as well as emissions from forest fires.

3 Methodology

Presented in this chapter is a detailed description of the methodology used in this work, which includes filter preparation, sampling, storage, extraction and analysis by gas chromatography – mass spectrometry (GC-MS).

3.1 Sampling Media Preparation

Prior to ambient sampling or coating 8 × 10 inch QFF (Pallflex Membrane Filters – 2500 QAT- Pall Life Sciences) and 5.6 × 5.4 inch slotted QFF (Staplex Slotted Media – TFAQ S810) were baked at temperatures of 1123 K and 973 K, respectively, in a muffle furnace (Fischer Scientific, Model 550-58) for 24 hours. This step was done in order to remove any organic impurities from the filters. After baking, these filters were stored in Pyrex glass container until used for sampling or coating with the adsorbent, Amberlite XAD-4TM (Sigma Aldrich).

3.1.1 XAD-4TM Resin Cleaning and Grinding

XAD-4TM, 20-60 mesh (Sigma Aldrich) was purchased from the supplier as a water-wet product, which also contains sodium chloride and sodium carbonate salts to prevent bacteria growth (Sigma-Aldrich Co., 1998). As such, the product required extensive cleaning prior to use. The cleaning procedure performed in this work was based on the method developed by Dr. Lane (Lane, private communication). In order to clean the resin, 500 g of the wet XAD-4TM resin was poured into a 300 mL beaker and methanol (Reagent grade, Sigma Aldrich) was added to the beaker while stirring until it

was approximately 1 mL above the resin surface. The XAD-methanol slurry was then placed in a Branson Ultrasonic Cleaner (Model 5510R-DTH) and sonicated for 30 minutes. Following the sonication, the slurry was filtered using a vacuum filtration system and was transferred to a clean 300 mL beaker. The sonication and filtration steps were then repeated with dichloromethane (Reagent grade, Sigma Aldrich) and hexane (Reagent grade, Sigma Aldrich) in the same manner as methanol. The resin was subsequently transferred to a clean Pyrex glass container and allowed to air-dry at room temperature for three weeks until the hexane was completely evaporated.

To enable the adsorbent to adhere to the surface of QFF, it was ground to a fine powder using a Retsch Planetary Ball Mill at Environment Canada. Two agate pots, each containing ten agate balls were first cleaned with Acetone. Each pot was then filled $\frac{3}{4}$ with the clean and dry XAD-4TM resin. The agate pots were then sealed with agate lids and placed in the planetary ball mill where the resin was ground for 34 hours at 400 rpm. Following the grinding, the ground resin was stored into a clean amber jar with a Teflon cap until used for coating.

3.1.2 Coating of 8 × 10 inch QFFs

The procedure used for coating QFFs in this project is based on methods developed by Gundel and Hering (1998) and Galarneau et al. (2006) with adjustments made by Busca (2010) and Saccon et al. (2013). A slurry of XAD-hexane with a concentration of approximately 22 g L⁻¹ was prepared in order to coat 12 QFFs (8 × 10 inch). The slurry was then poured into a thin layer chromatography (TLC) chamber containing ten glass plates. The TLC chamber was then placed into a sonic bath and sonicated for 30 minutes.

Stainless steel mesh (folded in a pocket form) was used as a filter holder for coating. The filters were then coated individually by dipping each filter ten times into the slurry. Once all the filters had been coated ten times they were allowed to dry while the slurry was sonicated for another 30 minutes. To ensure even coating of the filters, the filters were immersed in the slurry ten additional times in reverse order. The coated filters were then covered with clean aluminum foil and allowed to dry overnight. The following day, the coated filters were each rinsed with hexane in order to remove any excess XAD. The coated filters were then stored in a Pyrex glass container and covered with a Teflon sheet and a plastic lid until used for sampling.

3.2 Atmospheric Sampling

The ambient samples analyzed in this project were collected at two different locations, in Toronto, Ontario and close to Fort McMurray, Alberta. Sampling in Toronto was conducted between July 2013 and February 2015 on the roof of the Petrie Science and Engineering building at York University. These samples were used for concentration and phase distribution measurements of the selected classes of SVOCs in the atmosphere. Samples from Alberta were taken during the Oil Sands field campaign in summer 2013 at air monitoring station, AMS-13, approximately 35 km to the north of Fort McMurray (Figure 3.1). AMS-13 was operated by Environment Canada. This site is approximately 12 km to the north of two Oil Sands mining and processing sites, namely, Syncrude and Suncor and close to several tailing-ponds as well as open pit mines (Alberta Environment, c1995-2015). The objective of this field study was to characterize the type of SVOCs that are emitted and/or produced from the Oil Sands mining and related activities.

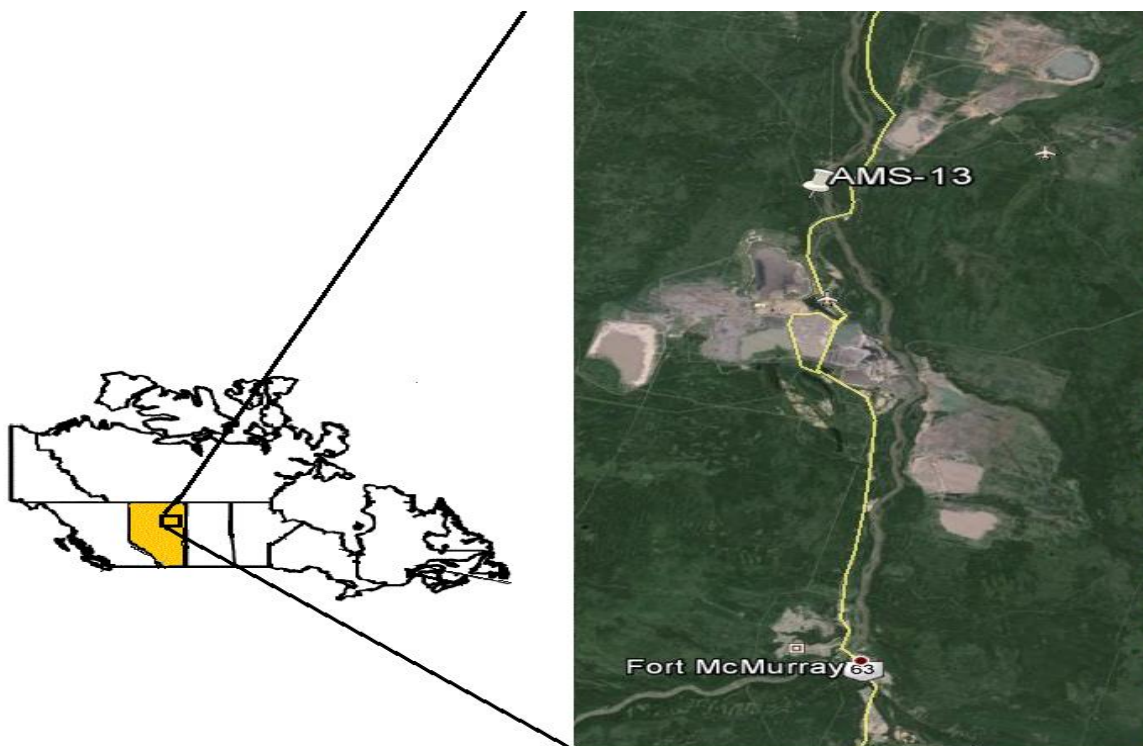


Figure 3.1: Satellite image of a portion of the Alberta Oil Sands region showing the location of the AMS-13 sampling site during the Alberta Oil Sands field campaign (Google map, June 16th 2015).

3.2.1 High Volume Air Sampling and Storage

Two types of high volume air samplers were used in this work for ambient sampling onto filters. The first type was a PM air sampler (TE-6001, Tisch Environmental, Inc.) equipped with a PM_{2.5} micron head, which contained 40 small impactor jets to remove particles with aerodynamic diameter larger than 2.5 μm . Two high volume air samplers of this type were used for ambient sampling at York University but only one was equipped with a flow recorder for calibration. The second type of high volume air sampler used was a single stage slotted impactor (TE-231, Tisch Environmental, Inc.), which was mainly used for sampling at the AMS-13 during the Alberta Oil Sands field campaign. This air sampler contained a 2.5 μm cut-off slotted

impactor, which was mounted onto a base plate and a slotted QFF was placed in between the two. The base plate was then mounted on an 8 × 10 inch filter holder as shown in Figure 3.2. As such, this air sampler allows simultaneous collection of both $PM > 2.5 \mu m$ and $PM \leq 2.5 \mu m$ on a slotted filter and 8 × 10 inch QFF, respectively. Due to technical difficulties, the slotted impactor setup was not applied to the high volume air sampler in the Oil Sands field campaign. As a result, total suspended particulate matter (TSP) and gas phase SVOCs were collected on the XAD-4TM SIF at AMS-13.

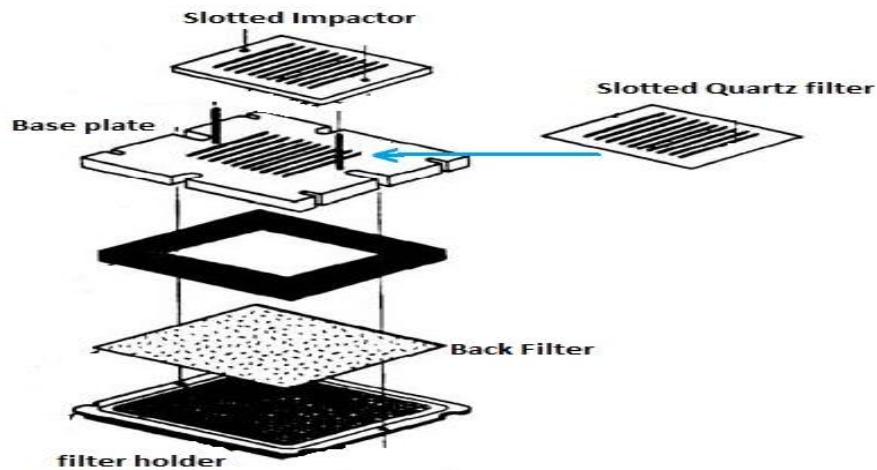


Figure 3.2: Assembly of the filters on the slotted impactor high volume air sampler (adapted from Tisch Environmental, Inc.).

Prior to sampling, the flow rate for the high volume air samplers was calibrated to standard flow rate of $1.13 \text{ m}^3 \text{ min}^{-1}$ using a calibration kit (TE-5028A, Tisch Environmental, Inc.). Since only one of the PM air samplers was equipped with a flow recorder, the flow rate of the sampler without the recorder was calibrated indirectly. To calibrate the air sampler with the recorder, a calibrator, which was equipped with a water manometer, was mounted onto the air sampler. The flow rate of the air sampler was then randomly set to five different values and the corresponding manometer and flow recorder

readings were taken at each flow rate. These readings were subsequently corrected for ambient pressure and temperature and used to plot a calibration curve. The equation of the line from the calibration curve was then used to determine the reading on the flow recorder, which corresponded to the standard flow rate of $1.13 \text{ m}^3 \text{ min}^{-1}$. Once the air sampler's flow rate was adjusted to the standard value, the reading on the manometer at this flow rate was used to calibrate the air sampler without the recorder. The slotted impactor high volume air sampler was equipped with a flow recorder and calibrated once before and during the field campaign using the procedure described above.

Typically, ambient samples were collected for a period of 24 hours corresponding to a total sampled air volume of 1627 m^3 . After sampling, the filters were stored individually in sealed mason jars and stored in a freezer at 253 K until analysis. The Oil Sands samples were stored in the same manner until they were transported to the laboratory at the end of the field campaign. During the transportation, the samples were kept in a cooler filled with ice packs. The samples arrived in the laboratory after five days and were stored in the freezer upon arrival. It should be noted that ice packs generally stay frozen from 24 to 36 hours in an insulated container. Since the samples arrived to the laboratory after five days a storage test was required (see section 4.1.5).

3.3 Sample Analysis

3.3.1 Solvents and Standard Reagents

All standards and solvents used in this work had a purity of 97 % to 99.8 % and were purchased from Sigma Aldrich or Supelco. The concentration of standard solutions of nitrophenols, n-alkanes and PAHs and their internal standards (IS) are shown in Tables 3.1, 3.2 and 3.3, respectively.

Table 3.1: Standard solution concentrations of target nitrophenols, IS, and volumetric standards (i.e. C₁₇, C₁₈, and C₁₉).

Compound	Abbreviation	Concentration of Standards (ng μL^{-1})
4-methyl-2-nitrophenol	4-me-2-NP	133
4-Nitrophenol	4-NP	101
3-methyl-4-nitrophenol	3-me-4-NP	103
2-methyl-4-nitrophenol	2-me-4-NP	108
2,6-dimethyl-4-nitrophenol	2,6-dime-4-NP	101
2-methyl-3-nitrophenol (IS)	2-me-3-NP	103
2-methyl-5-nitrophenol (IS)	2-me-5-NP	106
Heptadecane	C ₁₇	223
Octadecane	C ₁₈	229
Nonadecane	C ₁₉	209

Table 3.2: Standard solution concentrations of target n-alkanes and internal standard (IS).

Compound	Abbreviation	Concentration of Standards (ng μL^{-1})
Tridecane	C ₁₃	500 ^a , 100 ^b
Tetradecane	C ₁₄	500 ^a , 100 ^b
Pentadecane	C ₁₅	500 ^a , 100 ^b
Hexadecane	C ₁₆	500 ^a , 100 ^b
Heptadecane	C ₁₇	500 ^a , 100 ^b
Octadecane	C ₁₈	500 ^a , 100 ^b
Nonadecane	C ₁₉	500 ^a , 100 ^b
Eicosane	C ₂₀	500 ^a , 100 ^b
Heneicosane	C ₂₁	500 ^a , 100 ^b
Docosane	C ₂₂	500 ^a , 100 ^b
Tricosane	C ₂₃	500 ^a , 100 ^b
Tetracosane	C ₂₄	500 ^a , 100 ^b
Pentacosane	C ₂₅	500 ^a , 100 ^b
Nonadecane-D ₄₀ (IS)	C ₁₉ D ₄₀	1000 ^a , 100 ^b
Hexamethylbenzene	HMB	560

^a Standard stock solution for use in preparation of calibration mixture.

^b Standard mixture concentration used for recovery tests and extractions.

Table 3.3: Standard solution concentrations of target PAHs and internal standards (IS).

Compound	Abbreviation	Concentration of Standards (ng μL^{-1})
Naphthalene ⁽¹⁾	NAP	40 ^a , 50 ^b
Acenaphthylene ⁽²⁾	ACY	40 ^a , 50 ^b
Acenaphthene ⁽²⁾	ACE	40 ^a , 50 ^b
Fluorene ⁽²⁾	FLU	40 ^a , 50 ^b
Phenanthrene ⁽³⁾	PHE	40 ^a , 50 ^b
Anthracene ⁽³⁾	ANT	40 ^a , 50 ^b
Fluoranthene ⁽³⁾	FLT	40 ^a , 50 ^b
Pyrene ⁽³⁾	PYR	40 ^a , 50 ^b
Benz(a)anthracene ⁽⁴⁾	BaA	40 ^a , 50 ^b
Chrysene ⁽⁴⁾	CRY	40 ^a , 50 ^b
Benzo(b)fluoranthene ⁽⁴⁾	BbF	40 ^a , 50 ^b
Benzo(k)fluoranthene ⁽⁴⁾	BkF	40 ^a , 50 ^b
Benzo(a)pyrene ⁽⁴⁾	BaP	40 ^a , 50 ^b
Indeno(1,2,3-cd)pyrene ⁽⁴⁾	IND	40 ^a , 50 ^b
Dibenz(a,h)anthracene ⁽⁴⁾	dBahA	40 ^a , 50 ^b
Benzo(g,h,i)perylene ⁽⁴⁾	BghiP	40 ^a , 50 ^b
⁽¹⁾ Naphthalene-D ₈ (IS)	NAP-D ₈	500 ^a , 50 ^b
⁽²⁾ Acenaphthene-D ₁₀ (IS)	ACE-D ₁₀	500 ^a , 50 ^b
⁽³⁾ Phenanthrene-D ₁₀ (IS)	PHE-D ₁₀	500 ^a , 50 ^b
⁽⁴⁾ Chrysene-D ₁₂ (IS)	CRY-D ₁₂	500 ^a , 50 ^b
Hexamethylbenzene	HMB	560

Superscript numbers 1 to 4 indicate the respective internal standard (IS) used for each target PAH compound.

^a Standard stock solution for use in preparation of calibration mixture.

^b Standard mixture concentration used for recovery tests and extractions.

3.3.2 Extraction

The extraction procedure used in this work was adapted and modified from the method developed by Moukhtar et al. (2011) and Saccon et al. (2013). The filter sample (QFF or XAD-4TM SIF) was cut into eight pieces and seven pieces were placed in a 120 mL amber glass jar. The remaining filter piece was then spiked with approximately 4 μg of each of the nitrophenol internal standards, 2-me-3-NP and 2-me-5-NP, 1 or 4 μg of each of PAH internal standards, ACE-D₁₀, PHE-D₁₀, CHR-D₁₂, and NAP-D₈, and 4 or 15

μg of n-alkane internal standard, $\text{C}_{19}\text{D}_{40}$. The filter pieces were then fully immersed in approximately 20 mL of acetonitrile (Pestanal Grade, Sigma Aldrich) and mixed with a glass stirring rod. The jar containing the filter pieces was then placed in a sonic bath and sonicated for 15 minutes at room temperature.

After sonication, the solution was transferred using a pipette into a 20 mL glass syringe (Popper and Sons) equipped with a 0.20 μm Chromspec PTFE syringe filter (Chromatographic Specialties, Inc.) and was collected into a 250 mL round-bottom flask. The filter pieces were sonicated, extracted, and filtered three additional times into the same flask. The volume of the four combined extracts was then reduced from approximately 80 mL to 1 mL using a rotary evaporator with a water bath temperature of 316.15 K. The concentrated extract was subsequently transferred to a test tube and centrifuged for five minutes. At this point, the concentrated extract was divided evenly into two four-mL conical vials. One portion was used for PAH and n-alkane analysis while the other was used for nitrophenol analysis. The extract for the PAH and n-alkane analysis was further concentrated under a soft stream of ultra-high pure nitrogen (Grade 5.0, > 99 %, Linde) to a final volume of approximately 100 μL . The final extract was then spiked with 10 μL of volumetric standard, HMB (560 $\text{ng } \mu\text{L}^{-1}$), and divided evenly into two two-mL vials with a glass insert. One of these vials was immediately analyzed by GC-MS and the other was stored in a freezer. The volume of the extract fraction for nitrophenol analysis was then evaporated down to a final volume of approximately 220 μL by soft stream of nitrogen. This solution was subsequently transferred to a two-mL vial with a glass insert and underwent a series of sample cleanup steps.

3.3.3 HPLC Sample Clean-up for Nitrophenols

A Hewlett Packard 1050 high performance liquid chromatograph (HPLC) was used as a purification step to reduce the complexity of the ambient sample and possible peak overlap for concentration measurements of target nitrophenols. The HPLC instrument was equipped with a Supelco Supelcosil LC-18 column with dimensions of 25 cm × 4.6 mm and particle packing size of 5 μm. The detector used was a variable wavelength detector, which was set to 320 nm. A solvent gradient program was employed with two different solvents – Milli-Q water (18 MΩ) and acetonitrile; the solvent flow rate was set to a constant flow of 1 mL min⁻¹. The solvent gradient program started with 100 % deionized Milli-Q water and ended after 30 minutes with 100 % of acetonitrile. The target nitrophenol compounds and the internal standards eluted between 10 and 17 minutes and were collected in a clean flask.

3.3.4 Solid Phase Extraction for Nitrophenols

The effluent collected from the HPLC contained approximately equal amounts of water and acetonitrile. In order to remove the acetonitrile, the effluent's volume was reduced by a factor of two using a rotary evaporator at room temperature. A solvent exchange step was subsequently performed using solid phase extraction (SPE) using an Oasis hydrophilic-lipophilic balanced SPE cartridge, which was first conditioned with 1 mL of acetonitrile followed by 1 mL of Milli-Q water. The concentrated solution was acidified with 2 μL of dilute H₃PO₄ (pH ~ 1.8) and subsequently transferred into the cartridge. Once all of the solution had completely eluted from the cartridge, the phenols

were recovered from the SPE cartridge with approximately 10 mL of acetonitrile and the solution was collected into a clean flask. The volume of this solution was then evaporated down to approximately 1 mL using a rotary evaporator with water bath temperature of 316 K, and transferred into a conical vial. The extract volume in the vial was further reduced to approximately 100 μL , using a soft stream of nitrogen. The final extract was then spiked with 20 μL of volumetric standards C_{17} , C_{18} and C_{19} ($\sim 200 \text{ ng}/\mu\text{L}$). Half of this solution was saved in a glass vial for later use if needed and the other half was derivatized with 10 μL of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) prior to injection into the GC-MS. Figure 3.3 shows an example of derivatization reaction of BSTFA and 3-me-4-NP. After being derivatized, the solution was transferred into a vial with a glass insert and analyzed by GC-MS.

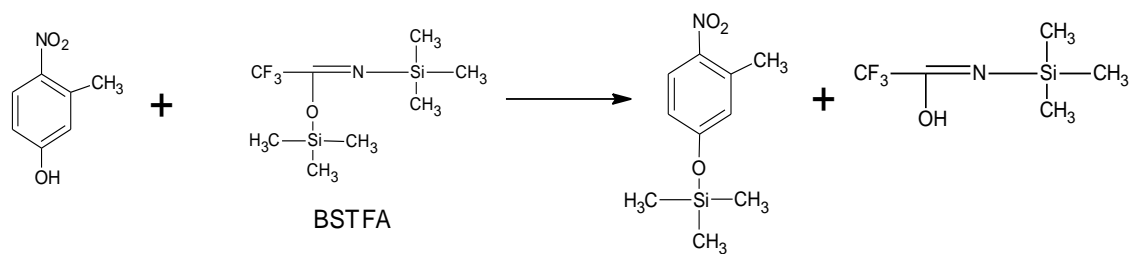


Figure 3.3: Derivatization reaction of 3-me-4-NP with BSTFA (adapted from Knapp, 1979).

3.3.5 Analysis by GC-MS

Concentration measurements of target nitrophenols, PAHs, and n-alkanes were obtained using a HP 5890 Series II gas chromatograph equipped with HP 5972 Series Mass Selective Detector (Figure 3.4). Following the extraction, 1 μL splitless injections were performed via a HP 6890 auto sampler. The carrier gas used was

Helium (5.0 grade, > 99.9 % purity, Linde) at a flow rate of 2 mL min⁻¹. The columns used were DB-5MS with column dimensions (60 m x 0.25 mm and 1.0 µm film thickness) or (60 m x 0.32 mm and 0.5 µm film thickness). The injection port and the detector temperatures used for nitrophenol analysis were set to 538 K and 553 K, respectively, but for PAHs/n-alkanes analysis the injection port temperature was changed to 563 K while the detector temperature was kept constant at 553 K. Two different temperature programs were used: one for nitrophenols (Figure 3.5) and another for PAHs/n-alkanes (Figure 3.6) analysis. Initially the temperature programs used for nitrophenols and PAHs/n-alkanes analysis were 132 and 142 minutes long, respectively, but were reduced to 60 and 95 minutes when the column was changed from one with 1µm film thickness to one with a smaller film thickness (0.5 µm). The acquisition mode used for sample analysis was either in scan mode or in selective ion monitoring mode (SIM) and each sample was run twice to check for reproducibility.

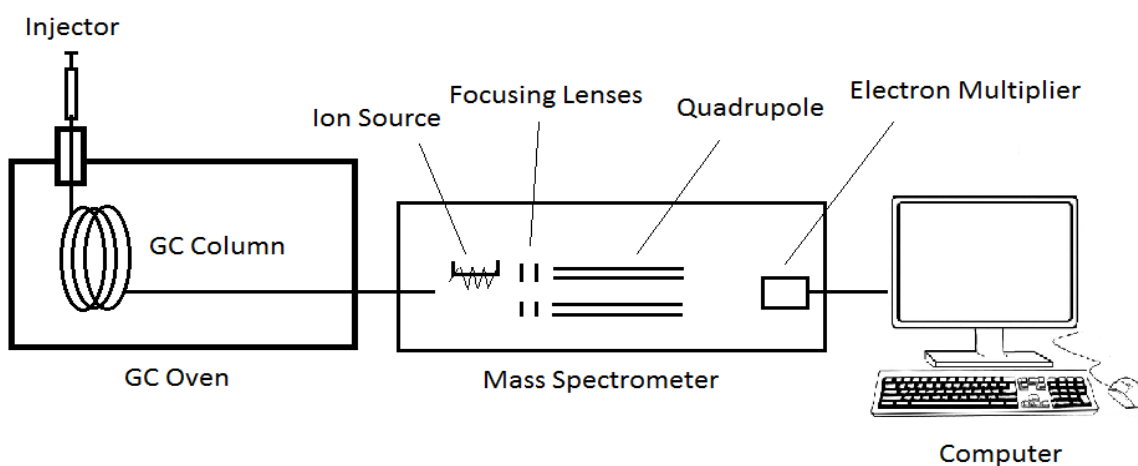


Figure 3.4: Schematic of the major instrumental setup of GC-MS.

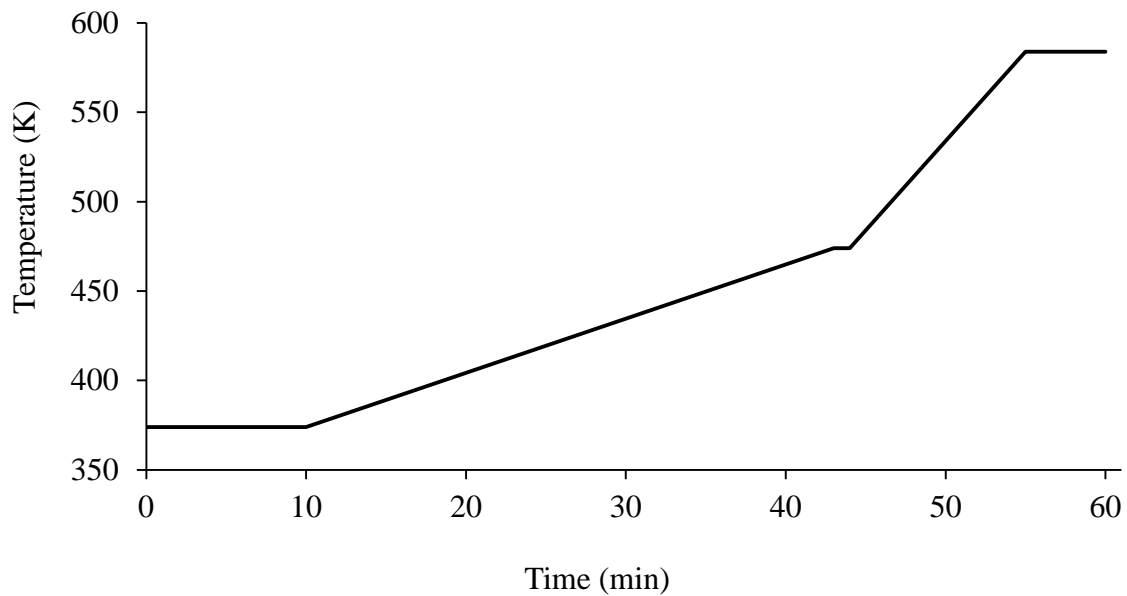


Figure 3.5: GC temperature program used for target nitrophenols analysis.

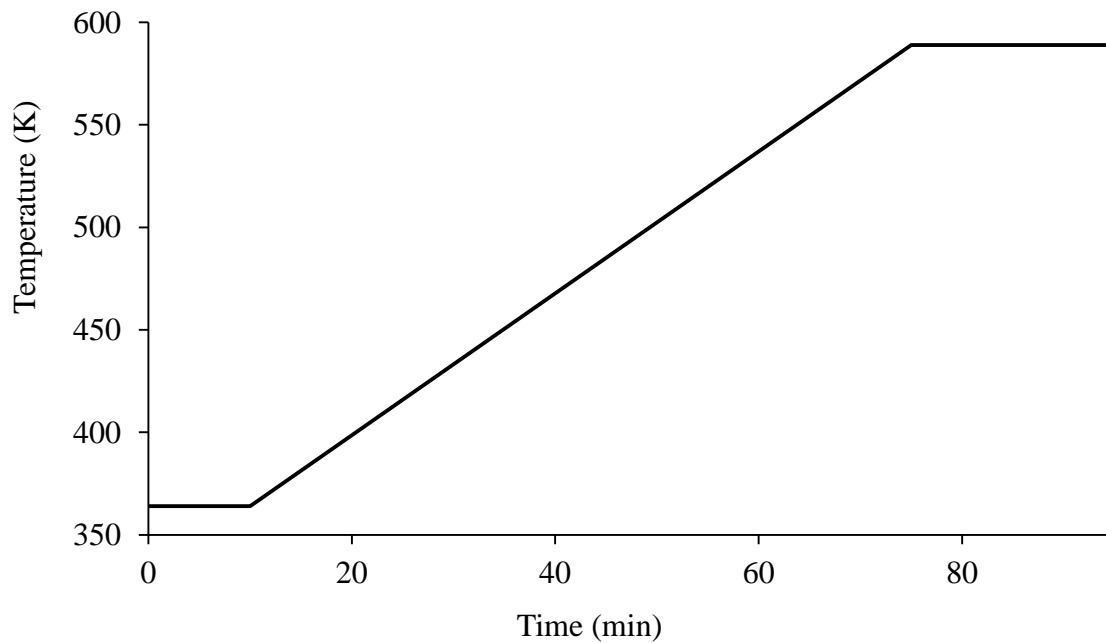


Figure 3.6: GC temperature program used for target PAHs and n-alkanes analysis.

3.3.6 Identification and Quantification of Target SVOCs by GC-MS

Target nitrophenol, n-alkane, and PAH compounds in spiked and ambient filters were identified using GC retention times and mass fragmentation patterns. For ambient samples, the target compound's retention time was compared to those from standard solutions. The monitored mass to charge ratios (m/z) used in SIM mode or scan mode along with GC retention times for each target nitrophenol, PAH/n-alkane compounds are summarized in Tables 3.4 and 3.5, respectively.

Table 3.4: GC retention time window for SIM and m/z ions monitored for target nitrophenols, internal standards and volumetric standards.

Compound	GC Retention Time Window (min)		Monitored m/z by SIM
	Column with 0.5 μm film thickness	Column with 1 μm film thickness	
4-me-2-NP	30-39	69-90	225, 210, 165
4-NP	30-39	69-90	211, 196, 150
3-me-4-NP	30-39	69-90	225, 210, 165
2-me-4-NP	30-39	69-90	225, 210, 165
2,6-dime-4-NP	40-60	91-132	239, 224
2-me-3-NP	30-39	69-90	225, 208, 165
2-me-5-NP	30-39	69-90	225, 210, 165
C ₁₇	40-60	91-132	85
C ₁₈	40-60	91-132	85
C ₁₉	40-60	91-132	85

Table 3.5: GC retention time and m/z ions monitored for target PAHs, n-alkanes, internal standards and volumetric standard^(a).

Compound	GC Retention Time (min)		Monitored m/z
	Column with 0.5 μm film thickness	Column with 1 μm film thickness	
NAP	19-23	31.7	129, 128
ACY	24-33	45.0	152, 151
ACE	34-36	46.5	154, 153
FLU	37-45	50.8	166, 165
PHE	46-48	58.8	178, 176
ANT	46-48	59.2	178, 176
FLT	56-61	50.8	202, 200
PYR	56-61	71.4	202, 200
BaA	62-74	86.8	228, 226
CRY	62-74	87.3	228, 226
BbF	75-82	104.0	252, 250
BkF	75-82	104.5	252, 250
BaP	75-82	109.4	252, 250
IND	83-95	127.4	277, 276
dBahA	83-95	127.9	279, 278
BghiP	83-95	131.6	277, 276
NAP-D ₈	19-23	31.5	136, 108
ACE-D ₁₀	34-36	46.1	164, 160
PHE-D ₁₀	46-48	58.5	189, 188
CRY-D ₁₂	62-74	86.8	240, 236
C ₁₃	24-33	34.4	85, 71
C ₁₄	24-33	39.2	85, 71
C ₁₅	34-36	43.6	85, 71
C ₁₆	37-45	47.8	85, 71
C ₁₇	37-45	51.7	85, 71
C ₁₈	46-48	55.4	85, 71
C ₁₉	49-55	59.0	85, 71
C ₂₀	49-55	62.3	85, 71
C ₂₁	56-61	65.6	85, 71
C ₂₂	56-61	69.1	85, 71
C ₂₃	62-74	73.1	85, 71
C ₂₄	62-74	77.4	85, 71
C ₂₅	62-74	82.1	85, 71
C ₁₉ D ₄₀	49-55	57.9	98, 82
HMB ^(a)	24-33	42.4	162, 147

In order to quantify target compounds in ambient samples and calibration mixtures, the sum of the peak areas of the specific ions monitored for each compound was calculated. This value was then used to determine the mass of a target nitrophenol or a PAH/n-alkane compound using Eq. 3.1 and 3.2, respectively. It is important to mention that for some low molecular mass (C₁₃ to C₁₅) and high molecular mass (C₂₄ and C₂₅) n-alkanes a compound specific correction was done using the ratio of the recovery relative to the recovery of the internal standard obtained for these compounds (Table 4.9). This was done due to the fact that C₁₉D₄₀ is highly substance specific and not sufficient to correct for all target n-alkanes.

$$m_T = \left(\frac{PA_T \times Cal_{IS}}{PA_{IS} \times Cal_T} \right) \times m_{IS_{Der}} \times \left(\frac{MM_T}{MM_{T_{Der}}} \right) \quad \text{Eq. (3.1)}$$

$$m_T = \left(\frac{PA_T \times Cal_{IS}}{PA_{IS} \times Cal_T} \right) \times m_{IS} \quad \text{Eq. (3.2)}$$

Here, m_T and m_{IS} are the masses of the target compound and internal standard, respectively. PA_T and PA_{IS} are the peak areas for the target compound and internal standard, respectively. The calibration response factor for target compounds and internal standards are presented as Cal_T and Cal_{IS} , respectively. MM_T is the molecular mass of the target compound. The superscript “Der” indicates a derivatized phenol compound or internal standard. The atmospheric concentration of a target compound was then calculated using Eq. 3.3.

$$C_T = \left(\frac{m_T - m_{blk}}{V} \right) \quad \text{Eq. (3.3)}$$

Here, C_T is the atmospheric concentration for the target compound, m_{blk} represents the blank mass and V is the sampling volume.

4 Results

This section will present the results from various tests performed to validate the suitability of XAD-4TM SIF analytical method for analysis of PAHs and n-alkanes followed by results obtained from analysis of ambient samples from Toronto and Oil Sands field campaign using the modified method.

4.1 Method Validation Tests

4.1.1 Blank Values and Detection Limits

Clean XAD-4TM SIFs and uncoated QFFs were tested for the presence of target PAHs, n-alkanes, and nitrophenols. These filters underwent the same extraction and analysis procedure described for ambient samples. In order to test if there was any blank value attributed to the transportation of XAD-4TM SIF to and from the Oil Sands sampling site, two field blanks were acquired. The field blank filters were transported to the sampling site and handled in the same way as other filters, but no ambient sample was collected on these filters. The results for both method and field blanks for nitrophenols are shown in Table 4.1. For target PAHs and n-alkanes the results of method and field blanks were not significantly different and were therefore combined and are shown in Tables 4.2 and 4.3, respectively. The equivalent atmospheric blank values were obtained by dividing the blank mass by 1627 m³, which is a typical 24-hour sampled volume.

Table 4.1: Method blank and standard deviation for target nitrophenols as well as the equivalent atmospheric concentration of method and field blanks on XAD-4TM SIFs. Here, n is the number of samples.

Compound	Method Blank n = 7			Field Blank 1	Field Blank 2
	Average Mass of Blank (ng)	Standard Deviation of Blank (ng)	High Volume Blank (ng m ⁻³)	High Volume Blank (ng m ⁻³)	High Volume Blank (ng m ⁻³)
4-me-2-NP	8.0	3.6	0.005	0.04	0.05
4-NP	83.5	53.4	0.07	0.02	0.03
3-me-4-NP	7.8	4.7	0.005	0.002	0.001
2-me-4-NP	16.6	14.4	0.01	0.0004	0.0003
2,6-dime-4-NP	3.0	2.1	0.002	0.0007	0.0009

Table 4.2: Blank mass, standard deviation and the equivalent atmospheric concentration for PAHs on XAD-4TM SIFs and uncoated QFF, here n is the number of samples.

Compound	XAD-4 TM SIF n = 7			QFF n = 1
	Average Mass of Blank (ng)	Standard Deviation of Blank (ng)	High Volume Blank (ng m ⁻³)	High Volume Blank (ng m ⁻³)
NAP	4823.2	1720.0	3.0	0.1
ACY	13.4	11.4	0.008	0.003
ACE	137.3	52.2	0.08	0.02
FLU	76.1	22.9	0.05	0.003
PHE	197.6	66.3	0.1	0.02
ANT	7.0	4.2	0.004	0.001
FLT	23.8	9.5	0.02	0.002
PYR	8.8	4.0	0.005	0.001
BaA	5.7	3.3	0.003	0.001
CRY	15.3	10.4	0.009	0.003
BbF	3.2	3.0	0.002	0.001
BkF	3.8	4.6	0.002	0.0004
BaP	23.3	13.3	0.01	0.001
IND	2.0	1.4	0.001	0.0004
dBahA	2.6	2.4	0.002	0.0004
BghiP	1.4	0.6	0.001	0.0004

Table 4.3: Blank mass, standard deviation and the equivalent atmospheric concentration for n-alkanes on XAD-4TM SIFs and uncoated QFF, here n is the number of samples.

Compound	XAD-4 TM SIF n = 6		QFF n = 1	
	Average Mass of Blank (ng)	Standard Deviation of Blank (ng)	High Volume Blank (ng m ⁻³)	High Volume Blank (ng m ⁻³)
C ₁₃	677.2	211.9	0.4	0.1
C ₁₄	2110.3	595.9	1.3	0.05
C ₁₅	2373.6	1348.1	1.5	0.1
C ₁₆	2722.9	1288.4	1.7	0.2
C ₁₇	2721.9	1193.0	1.7	0.3
C ₁₈	1947.0	782.1	1.2	0.4
C ₁₉	892.4	309.5	0.5	0.2
C ₂₀	648.1	200.7	0.4	0.2
C ₂₁	358.1	100.4	0.2	0.1
C ₂₂	459.4	181.1	0.3	0.2
C ₂₃	412.7	162.7	0.3	0.1
C ₂₄	455.9	219.3	0.3	0.07
C ₂₅	410.7	202.8	0.3	0.04

Detection limits for all target compounds were determined using three times the standard deviation of the XAD-4TM SIF blank values. The detection limit results for nitrophenols, PAHs, and n-alkanes are summarized in Tables 4.4 and 4.5, respectively.

Table 4.4: Detection limits (DL) and atmospheric detection limits for nitrophenols.

Compound	DL (ng)	High Volume DL (ng m ⁻³)
4-me-2-NP	10.8	0.007
4-NP	160.1	0.1
3-me-4-NP	14.0	0.009
2-me-4-NP	42.2	0.03
2,6-dime-4-NP	6.4	0.004

Table 4.5: Detection limits (DL) and atmospheric detection limits for PAHs and n-alkanes.

PAH	DL (ng)	High Volume DL (ng m ⁻³)	n-Alkane	DL (ng)	High Volume DL (ng m ⁻³)
NAP	5159.9	3.2	C ₁₃	635.6	0.4
ACY	34.2	0.02	C ₁₄	1787.6	1.1
ACE	156.6	0.1	C ₁₅	4044.3	2.5
FLU	68.6	0.04	C ₁₆	3865.2	2.4
PHE	199.0	0.1	C ₁₇	3579.1	2.2
ANT	12.7	0.008	C ₁₈	2346.4	1.4
FLT	28.5	0.02	C ₁₉	928.4	0.6
PYR	12.0	0.007	C ₂₀	602.1	0.4
BaA	9.9	0.006	C ₂₁	301.1	0.2
CRY	31.1	0.02	C ₂₂	543.3	0.3
BbF	9.0	0.006	C ₂₃	488.2	0.3
BkF	13.9	0.009	C ₂₄	657.9	0.4
BaP	39.8	0.02	C ₂₅	608.3	0.4
IND	4.1	0.003			
dBahA	7.3	0.005			
BghiP	1.9	0.001			

4.1.2 GC-MS Calibration

Prior to sample analysis, GC-MS was regularly calibrated with each class of SVOC separately by injecting five standard solutions at varying concentrations, each containing all target compounds, internal standards, and volumetric standards. The calibration concentration ranges used were 1 to 15 ng μL^{-1} for PAHs, 1 to 10 ng μL^{-1} for nitrophenols, and 5 to 75 ng μL^{-1} for n-alkanes. The results from the five point concentration levels were then used to plot a calibration curve for each target compound, an example of which is shown in (Figure 4.1). GC-MS calibration was run once a month or after the ion source was cleaned. For quality control, a mid-range concentration level standard was run approximately every ten runs.

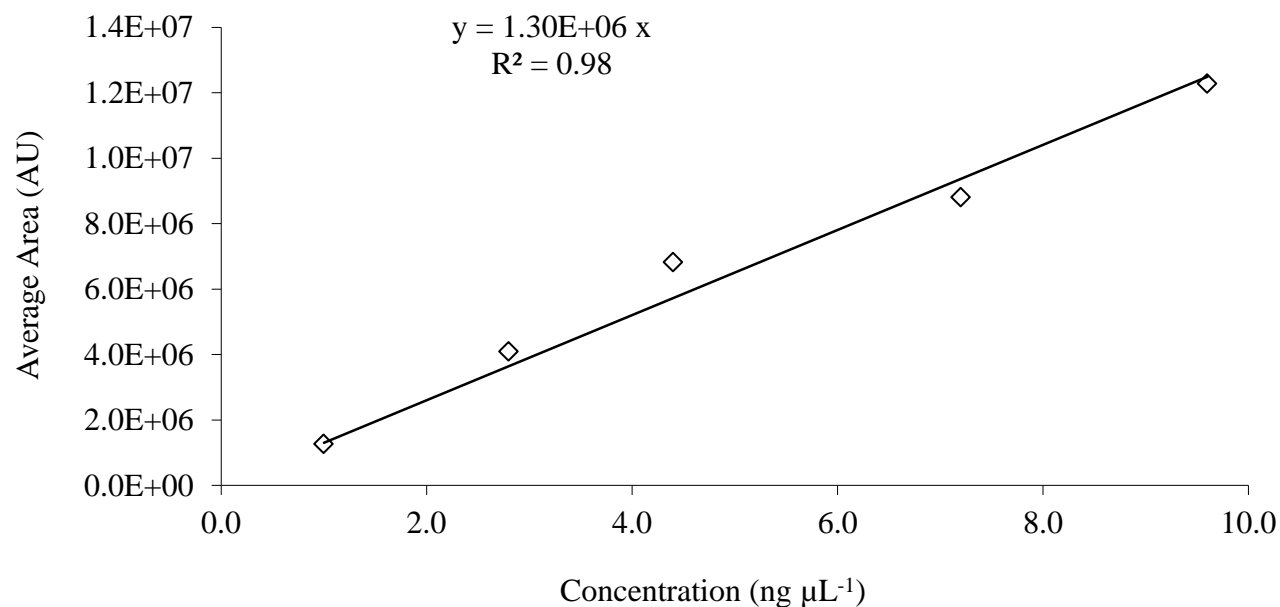


Figure 4.1: An example of calibration curve for phenanthrene.

4.1.3 Measurement Precision

All samples and calibration mixtures were run twice by GC-MS. In order to determine the precision of the duplicate measurements the ratio of the target compound peak area to that of internal standard peak area was calculated for each run. The differences in ratios between the first and second runs were calculated individually for all compounds for all measurements. The standard deviation (SD) of these differences was then calculated and the uncertainty of the repeat measurements (σ_{rpd}) was determined using Eq. 4.1. The results are summarized in Tables 4.6 and 4.7 for nitrophenols and PAHs/n-alkanes, respectively.

$$\sigma_{rpd} = SD \sqrt{2} \quad \text{Eq. 4.1}$$

Table 4.6: Individual uncertainty of GC-MS measurements (σ_{rpd}) for target nitrophenols relative to internal standards.

Compound	σ_{rpd} (%)	
	2-me-3-NP	2-me-5-NP
4-me-2-NP	10.0	7.2
4-NP	16.1	14.8
3-me-4-NP	2.3	1.8
2-me-4-NP	4.2	2.3
2,6-dime-4-NP	1.0	0.8
Average	6.7	5.4

Table 4.7: Individual uncertainties of GC-MS measurements (σ_{rpd}) for all target PAHs and n-alkanes relative to internal standards.

PAH	σ_{rpd} (%)	n-Alkane	σ_{rpd} (%)
NAP	33.4	C ₁₃	17.4
ACY	7.7	C ₁₄	26.8
ACE	13.3	C ₁₅	28.9
FLU	20.6	C ₁₆	26.0
PHE	21.2	C ₁₇	22.0
ANT	8.3	C ₁₈	28.4
FLT	11.4	C ₁₉	27.3
PYR	12.6	C ₂₀	16.6
BaA	13.2	C ₂₁	10.6
CRY	7.8	C ₂₂	12.0
BbF	6.9	C ₂₃	11.7
BkF	2.0	C ₂₄	10.7
BaP	3.2	C ₂₅	5.0
IND	3.0		
dBahA	2.7		
BghiP	2.7		
Average	10.6		18.7

4.1.4 Extraction Efficiency of PAHs and n-Alkanes on XAD-4TM SIF

To examine the extraction efficiency of PAH and n-alkane compounds on XAD-4TM SIFs, tests were performed where clean XAD-4TM coated filters were spiked with known masses of PAHs and n-alkanes. Spiked filters were subsequently extracted and analyzed by the same extraction procedure outlined for ambient samples. The recovery yields were then calculated using Eq. 4.2, where m_{recov} and m_{spk} are the masses of the target compound recovered and spiked, respectively.

$$\text{Recovery yield} = \frac{m_{\text{recov}}}{m_{\text{spk}}} * 100 \% \quad \text{Eq. (4.2)}$$

The initial mass of the target compound on the filter can be determined from the previously spiked internal standard, but not the mass recovered. In order to determine the recovered mass of the target compound in the final extract, a volumetric standard was spiked into the concentrated extract prior to GC-MS analysis. The recovery yields as well as the recoveries relative to the recovery of the selected internal standards of spiked PAHs and n-alkanes are shown in Table 4.8.

Table 4.8: Average recovery yields of PAHs and n-alkanes from XAD-4TM SIFs that were spiked with 1 μg of target PAHs and 4 μg of target n-alkanes, respectively. The errors shown here are the standard deviations of the measurements. Here n is the number of samples.

Compound	Recovery (%)	Recovery relative to IS
n = 4		
NAP-D ₈ (IS)	45 ± 2	
NAP	N/A	N/A
ACE-D ₁₀ (IS)	60 ± 10	
ACY	61 ± 7	1.1 ± 0.2
ACE	48 ± 6	0.9 ± 0.2
FLU	59 ± 3	1.1 ± 0.2
PHE-D ₁₀ (IS)	63 ± 20	
PHE	52 ± 10	0.9 ± 0.2
ANT	69 ± 9	1.2 ± 0.3
FLT	59 ± 10	1.0 ± 0.3
PYR	57 ± 8	1.0 ± 0.3
CRY-D ₁₂ (IS)	59 ± 12	
BaA	68 ± 9	1.2 ± 0.3
CRY	60 ± 12	1.0 ± 0.2
BbF	61 ± 8	1.1 ± 0.2
BkF	61 ± 14	1.0 ± 0.2
BaP	67 ± 13	1.2 ± 0.3
IND	54 ± 11	1.0 ± 0.3
dBahA	59 ± 12	1.0 ± 0.3
BghiP	43 ± 8	0.7 ± 0.2
n = 3		
C ₁₉ D ₄₀ (IS)	60 ± 11	
C ₁₃	13 ± 3	0.22 ± 0.01
C ₁₄	22 ± 11	0.4 ± 0.2
C ₁₅	40 ± 15	0.7 ± 0.2
C ₁₆	44 ± 17	0.7 ± 0.2
C ₁₇	77 ± 20	1.3 ± 0.2
C ₁₈	71 ± 12	1.2 ± 0.2
C ₁₉	76 ± 11	1.3 ± 0.2
C ₂₀	66 ± 11	1.12 ± 0.08
C ₂₁	59 ± 15	0.98 ± 0.07
C ₂₂	50 ± 13	0.84 ± 0.06
C ₂₃	45 ± 10	0.76 ± 0.09
C ₂₄	33 ± 11	0.54 ± 0.08
C ₂₅	19 ± 9	0.3 ± 0.1

NA: not available.

4.1.5 Storage Test for Oil Sands Samples

Ambient samples from the Oil Sands field campaign were transported and arrived to the laboratory after a period of five days. Although samples were stored in a cooler filled with ice packs during the transportation, they were outside the freezer longer than expected. To examine if there were any losses due to storage outside the freezer, two blank filters were spiked with each of the target compounds and internal standards and were stored in a glass jar at room temperature for a period of five days. Each filter was then extracted and analyzed. The results of this test are shown in Tables 4.9 and 4.10 for nitrophenols and PAHs/n-alkanes, respectively.

Table 4.9: Recovery yields of nitrophenols from two XAD-4TM SIFs that were each spiked with 4 µg of each target compound and internal standard, stored at room temperature for five days and analyzed.

Compound	Recovery (%)	
	Test 1	Test 2
4-me-2-NP	42	38
4-NP	44	39
3-me-4-NP	58	50
2-me-4-NP	66	52
2,6-dime-4-NP	21	12
2-me-3-NP	73	50
2-me-5-NP	73	55

Table 4.10: Recovery yields of PAHs and n-alkanes from two XAD-4TM SIFs. Each filter was spiked with 4 µg of each of the target n-alkanes and internal standard as well as 1 µg of each of the target PAHs and internal standards, stored at room temperature for five days and analyzed.

PAH	Recovery (%)		n-Alkane	Recovery (%)	
	Test 1	Test 2		Test 1	Test 2
NAP	69	58	C ₁₃	6	7
ACY	65	58	C ₁₄	11	5
ACE	69	59	C ₁₅	4	3
FLU	60	51	C ₁₆	5	3
PHE	72	64	C ₁₇	6	4
ANT	59	52	C ₁₈	52	55
FLT	54	47	C ₁₉	44	47
PYR	54	47	C ₂₀	47	47
BaA	51	42	C ₂₁	49	45
CRY	59	49	C ₂₂	50	41
BbF	52	47	C ₂₃	53	40
BkF	58	52	C ₂₄	37	22
BaP	74	64	C ₂₅	25	14
IND	67	68	C ₁₉ D ₄₀	48	55
dBahA	63	55			
BghiP	69	58			
NAP-D ₈	58	53			
ACE-D ₁₀	66	67			
PHE-D ₁₀	85	85			
CRY-D ₁₂	57	61			

4.1.6 XAD-4™ SIF Sampling Efficiency

To test the sampling efficiency of XAD-4™ SIF for PAHs and n-alkanes, two XAD-4™ SIFs were sampled in series by placing one filter over the other and inserting an 8 × 10 inch piece of stainless steel mesh in between. Each filter was then extracted and analyzed separately using the same extraction procedure explained for ambient samples. The sampling efficiency of the target compounds was calculated using Eq. 4.3 to determine if there was any breakthrough onto the second filter. The results of this test are shown in Tables 4.11 and 4.12.

$$\text{Sampling Efficiency (\%)} = \frac{Mass_{top\ filter}}{(Mass_{top\ filter} + Mass_{bottom\ filter})} \times 100 \% \quad \text{Eq. (4.3)}$$

Table 4.11: Collection efficiency of XAD-4™ SIF for n-alkanes.

Compound	Test 1			Test 2		
	Top Filter (ng m ⁻³)	Bottom Filter (ng m ⁻³)	Percentage on Top Filter (%)	Top Filter (ng m ⁻³)	Bottom Filter (ng m ⁻³)	Percentage on Top Filter (%)
C ₁₃	64.2	14.6	81	47.3	7.0	87
C ₁₄	84.6	7.2	92	77.9	3.6	96
C ₁₅	48.0	< 2.5	> 95	38.1	< 2.5	> 94
C ₁₆	28.4	< 2.4	> 92	24.0	< 2.4	> 91
C ₁₇	10.0	< 2.2	> 82	9.6	< 2.2	> 81
C ₁₈	14.1	< 1.4	> 91	5.7	< 1.4	> 80
C ₁₉	3.2	< 0.6	> 85	4.0	< 0.6	> 88
C ₂₀	2.0	< 0.5	> 81	3.4	< 0.5	> 88
C ₂₁	1.8	< 0.2	> 88	2.2	< 0.2	> 90
C ₂₂	1.6	< 0.4	> 80	1.7	< 0.4	> 81
C ₂₃	1.4	< 0.3	> 80	1.4	< 0.3	> 80
C ₂₄	1.6	< 0.4	> 79	< 0.4	< 0.4	NA
C ₂₅	2.9	0.5	85	1.0	< 0.4	> 72

Table 4.12: Collection efficiency of XAD-4TM SIF for PAHs.

Compound	Test 1			Test 2		
	Top Filter (ng m ⁻³)	Bottom Filter (ng m ⁻³)	Percentage on Top Filter (%)	Top Filter (ng m ⁻³)	Bottom Filter (ng m ⁻³)	Percentage on Top Filter (%)
NAP	< 3.3	< 3.2	NA	< 3.3	< 3.3	NA
ACY	0.4	< 0.02	> 95	0.1	< 0.02	> 82
ACE	1.5	0.83	65	2.5	0.4	86
FLU	2.4	0.35	87	2.3	< 0.04	> 98
PHE	3.6	0.14	96	2.9	0.02	99
ANT	0.03	< 0.008	> 80	0.08	< 0.008	> 91
FLT	0.5	0.02	96	0.4	< 0.02	> 95
PYR	0.2	0.01	95	0.2	< 0.007	> 97
BaA	< 0.006	< 0.006	NA	0.05	< 0.006	> 89
CRY	< 0.02	< 0.02	NA	0.07	< 0.02	> 79
BbF	< 0.006	< 0.006	NA	0.07	< 0.006	> 93
BkF	< 0.009	< 0.009	NA	0.03	< 0.009	> 74
BaP	< 0.02	< 0.02	NA	< 0.02	< 0.02	NA
IND	< 0.003	< 0.003	NA	0.03	< 0.003	> 92
dBahA	< 0.005	< 0.005	NA	< 0.005	< 0.005	NA
BghiP	< 0.001	< 0.001	NA	0.04	< 0.001	> 97

NA: not available.

4.1.7 Parallel Sampling Reproducibility

XAD-4TM SIFs and uncoated QFFs were sampled in parallel, using two separate high-volume air samplers. This sampling technique was employed for phase partitioning measurements. To validate the reproducibility of parallel sampling, a test was performed where three QFFs underwent sample collection in parallel using three separate high volume air samplers. Prior to sampling, the flow rates of the three air samples were calibrated to the standard flow rate of 1.13 m³ min⁻¹ using the procedure described in section 3.2.1. Following the sample collection, each filter was extracted and analyzed separately and the results are summarized in Table 4.13.

Table 4.13: Ambient concentrations of the target nitrophenols obtained from each QFF using different high volume air samplers, average \pm standard deviation and the relative standard deviation (RSD).

Compound	PM high volume air sampler-A	PM high volume air sampler-B	PM _{2.5} slotted impactor high volume sampler	Average	RSD (%)
ng m ⁻³					
4-me-2-NP	< DL	< DL	< DL	< DL	< DL
4-NP	0.42 \pm 0.07	0.49 \pm 0.08	0.6 \pm 0.1	0.51 \pm 0.08	15
3-me-4-NP	0.040 \pm 0.001	0.033 \pm 0.001	0.049 \pm 0.001	0.041 \pm 0.007	17
2-me-4-NP	0.084 \pm 0.002	0.065 \pm 0.002	0.091 \pm 0.003	0.07 \pm 0.01	17
2,6-dime-4-NP	0.010 \pm 0.001	0.013 \pm 0.001	0.019 \pm 0.001	0.014 \pm 0.004	27

4.1.8 Nitrophenols in PM_{2.5}

The high volume air samplers employed for concentration measurements of phenols in previous studies by our group were typically setup to collect particles in the size range of 2.5 μ m and smaller, only. To examine the extent to which these compounds are found in PM larger than 2.5 μ m, ambient samples were collected using a slotted impactor high volume air sampler, since it allows simultaneous collection of both PM > 2.5 μ m and PM \leq 2.5 μ m. A slotted QFF was used to collect nitrophenols in PM > 2.5 μ m and a XAD-4TM SIF for collection of total – PM \leq 2.5 μ m and gas phase nitrophenols. Each filter was then extracted and analyzed separately and the results are summarized in Table 4.14. The percentage of nitrophenols (NP) found on PM > 2.5 microns was calculated using Eq. 4.4.

$$\text{Percent NP on } PM_{>2.5} = \frac{NP \text{ mass on } PM_{>2.5}}{(NP \text{ mass on } PM_{\leq 2.5} + NP \text{ mass on } PM_{>2.5})} \times 100 \% \quad \text{Eq. (4.4)}$$

Table 4.14: Percentage of nitrophenols found on PM larger than 2.5 μm .

Compound	ng m ⁻³		Percentage in PM > 2.5 (%)
	TSP + Gas Phase	PM _{>2.5}	
4-me-2-NP	0.7	< 0.007	< 0.9
4-NP	10.4	0.3	3.1
3-me-4-NP	1.1	0.03	2.8
2-me-4-NP	2.0	0.05	2.4
2,6-dime-4-NP	0.6	0.004	0.7

4.2 Ambient Sampling

4.2.1 SVOCs Concentration Measurements from Oil Sands Samples

The results obtained from seven Oil Sands samples are summarized in Tables 4.15, 4.16 and 4.17 for nitrophenols, n-alkanes, and PAHs, respectively. These samples were taken between September 1st and 9th in the Oil Sands region at AMS-13.

Table 4.15: Summary of the ambient concentrations of total (gas phase and TSP) nitrophenols obtained from seven Oil Sands samples.

Compound	Concentration (ng m ⁻³)						
	Sep. 1 st	Sep. 2 nd	Sep. 4 th	Sep. 6 th	Sep. 7 th	Sep. 8 th	Sep. 9 th
4-me-2-NP	0.06 ± 0.01	0.10 ± 0.01	0.27 ± 0.03	0.15 ± 0.02	< DL	0.031 ± 0.008	0.19 ± 0.03
4-NP	0.39 ± 0.07	0.66 ± 0.08	7.1 ± 0.9	1.1 ± 0.1	1.5 ± 0.2	1.3 ± 0.3	0.45 ± 0.08
3-me-4-NP	0.032 ± 0.009	0.021 ± 0.004	0.37 ± 0.05	0.09 ± 0.01	0.10 ± 0.02	0.04 ± 0.01	0.03 ± 0.01
2-me-4-NP	< DL	0.11 ± 0.01	1.9 ± 0.2	0.44 ± 0.06	0.52 ± 0.08	0.23 ± 0.06	< DL
2,6-dime-4-NP	0.025 ± 0.006	0.065 ± 0.008	0.8 ± 0.1	0.14 ± 0.02	0.29 ± 0.05	0.028 ± 0.008	0.010 ± 0.005

< DL: concentrations that were less than the detection limit.

Table 4.16: Summary of the ambient concentrations of total (gas phase and TSP) n-alkanes obtained from seven Oil Sands samples.

Compound	Concentration (ng m ⁻³)						
	Sep. 1 st	Sep. 2 nd	Sep. 4 th	Sep. 6 th	Sep. 7 th	Sep. 8 th	Sep. 9 th
C ₁₃	2.8 ± 0.8	7 ± 1	11 ± 3	1.5 ± 0.3	52 ± 9	11 ± 2	7 ± 2
C ₁₄	38 ± 10	43 ± 12	55 ± 15	8 ± 2	390 ± 106	5 ± 2	11 ± 3
C ₁₅	35 ± 10	39 ± 11	57 ± 17	13 ± 4	159 ± 46	11 ± 4	12 ± 4
C ₁₆	16 ± 4	15 ± 4	21 ± 6	5 ± 2	62 ± 16	6 ± 2	5 ± 2
C ₁₇	5 ± 1	6 ± 1	9 ± 3	6 ± 1	18 ± 4	5 ± 1	5 ± 1
C ₁₈	4 ± 1	3.0 ± 0.9	7 ± 2	5 ± 1	5 ± 2	4 ± 1	2.1 ± 0.8
C ₁₉	7 ± 2	2.3 ± 0.6	8 ± 2	2.9 ± 0.8	2.4 ± 0.7	3.1 ± 0.9	4 ± 1
C ₂₀	2.7 ± 0.5	1.1 ± 0.2	3.9 ± 0.8	2.9 ± 0.5	1.5 ± 0.3	2.9 ± 0.5	3.3 ± 0.6
C ₂₁	2.8 ± 0.3	1.1 ± 0.1	3.0 ± 0.4	2.8 ± 0.3	1.3 ± 0.2	3.3 ± 0.4	4.0 ± 0.5
C ₂₂	1.6 ± 0.2	0.8 ± 0.1	2.1 ± 0.4	2.0 ± 0.3	0.9 ± 0.2	2.2 ± 0.3	2.9 ± 0.5
C ₂₃	2.8 ± 0.4	1.3 ± 0.2	2.4 ± 0.4	2.4 ± 0.3	0.8 ± 0.1	3.3 ± 0.4	4.5 ± 0.6
C ₂₄	2.7 ± 0.4	1.1 ± 0.2	3.7 ± 0.9	1.2 ± 0.2	1.8 ± 0.3	2.7 ± 0.4	4.3 ± 0.8
C ₂₅	3.9 ± 0.5	4.4 ± 0.5	4 ± 1	1.0 ± 0.1	1.6 ± 0.4	5.9 ± 0.6	11 ± 1

Table 4.17: Summary of the ambient concentrations of total (gas phase and TSP) PAHs obtained from seven Oil Sands samples.

Compound	Concentration (ng m ⁻³)						
	Sep. 1 st	Sep. 2 nd	Sep. 4 th	Sep. 6 th	Sep. 7 th	Sep. 8 th	Sep. 9 th
NAP	< DL	< DL	< DL	< DL	< DL	< DL	< DL
ACY	< DL	< DL	< DL	< DL	< DL	0.10 ± 0.01	< DL
ACE	0.5 ± 0.1	0.7 ± 0.1	0.8 ± 0.2	0.27 ± 0.06	0.18 ± 0.05	0.05 ± 0.03	0.8 ± 0.2
FLU	0.7 ± 0.1	0.6 ± 0.1	2.5 ± 0.5	0.7 ± 0.1	0.6 ± 0.1	0.5 ± 0.1	0.41 ± 0.09
PHE	1.7 ± 0.4	1.1 ± 0.2	11 ± 2	1.3 ± 0.3	1.6 ± 0.4	1.6 ± 0.4	1.0 ± 0.2
ANT	< DL	< DL	< DL	0.021 ± 0.003	0.13 ± 0.02	0.019 ± 0.003	< DL
FLT	0.11 ± 0.02	0.03 ± 0.01	0.49 ± 0.07	0.10 ± 0.01	0.10 ± 0.01	0.18 ± 0.02	< DL
PYR	0.17 ± 0.02	0.05 ± 0.01	0.59 ± 0.09	0.15 ± 0.02	0.11 ± 0.02	0.19 ± 0.03	0.12 ± 0.02
BaA	0.009 ± 0.002	< DL	0.05 ± 0.01	0.09 ± 0.01	0.021 ± 0.004	0.13 ± 0.02	0.02 ± 0.01
CRY	0.02 ± 0.01	< DL	0.04 ± 0.01	0.03 ± 0.01	0.04 ± 0.01	0.020 ± 0.005	0.03 ± 0.01
BbF	< DL	< DL	0.07 ± 0.01	0.012 ± 0.002	0.014 ± 0.002	0.009 ± 0.002	< DL
BkF	< DL	< DL	0.02 ± 0.01	< DL	< DL	< DL	< DL
BaP	< DL	< DL	< DL	< DL	< DL	< DL	< DL
IND	< DL	0.006 ± 0.001	0.07 ± 0.01	< DL	< DL	< DL	< DL
dBahA	< DL	< DL	< DL	< DL	< DL	< DL	< DL
BghiP	< DL	0.006 ± 0.001	0.07 ± 0.01	0.006 ± 0.001	0.008 ± 0.001	< DL	< DL

< DL: concentrations that were less than the detection limit.

4.2.2 SVOCs Concentration Measurements from Toronto Samples

The total (gas phase and PM) ambient concentrations for nitrophenols, n-alkanes, and PAHs for Toronto samples are shown in Tables 4.18, 4.19 and 4.20, respectively.

Table 4.18: Summary of the ambient concentrations of total (gas phase and PM_{2.5}) nitrophenols obtained from Toronto samples.

Compound	Concentration (ng m ⁻³)				
	July 23 rd 2013	Jan. 13 th 2014	Dec. 12 th 2013	Feb. 16 th 2015	Feb. 23 rd 2015
4-me-2-NP	0.02 ± 0.01	0.71 ± 0.06	2.2 ± 0.2	12 ± 1	15 ± 1
4-NP	2.3 ± 0.4	10 ± 2	17 ± 3	18 ± 3	20 ± 3
3-me-4-NP	0.09 ± 0.01	1.02 ± 0.02	1.85 ± 0.04	4.22 ± 0.09	4.57 ± 0.09
2-me-4-NP	0.35 ± 0.03	1.92 ± 0.06	1.63 ± 0.05	9.0 ± 0.3	6.7 ± 0.2
2,6-dime-4-NP	0.095 ± 0.004	0.62 ± 0.01	0.432 ± 0.004	2.79 ± 0.03	0.98 ± 0.01

Table 4.19: Summary of the ambient concentrations of total (gas phase and PM_{2.5}) n-alkanes obtained from Toronto samples.

Compound	Concentration (ng m ⁻³)				
	July 23 rd 2013	Oct. 29 th 2013	Dec. 12 th 2013	Feb. 16 th 2015	Feb. 23 rd 2015
C ₁₃	64 ± 11	47 ± 8	18 ± 3	231 ± 41	47 ± 8
C ₁₄	85 ± 23	78 ± 21	29 ± 8	286 ± 78	67 ± 18
C ₁₅	48 ± 14	38 ± 11	15 ± 4	85 ± 25	24 ± 7
C ₁₆	28 ± 8	24 ± 6	10 ± 3	39 ± 10	12 ± 3
C ₁₇	10 ± 2	10 ± 2	5 ± 1	11 ± 3	4 ± 1
C ₁₈	14 ± 4	6 ± 2	2.7 ± 0.8	6 ± 2	1.8 ± 0.6
C ₁₉	3.2 ± 0.9	4 ± 1	0.9 ± 0.3	4 ± 1	1.1 ± 0.3
C ₂₀	2.0 ± 0.4	3.5 ± 0.6	0.6 ± 0.1	2.9 ± 0.5	0.7 ± 0.2
C ₂₁	1.8 ± 0.2	2.2 ± 0.3	0.6 ± 0.1	1.2 ± 0.2	0.5 ± 0.1
C ₂₂	1.6 ± 0.2	1.7 ± 0.2	0.6 ± 0.1	0.6 ± 0.1	< DL
C ₂₃	1.4 ± 0.2	1.4 ± 0.2	0.5 ± 0.1	< DL	< DL
C ₂₄	1.6 ± 0.3	< DL	1.1 ± 0.3	< DL	< DL
C ₂₅	2.9 ± 0.4	1.0 ± 0.4	1.6 ± 0.4	1.0 ± 0.4	0.6 ± 0.3

< DL: concentrations that were less than the detection limit.

Table 4.20: Summary of the ambient concentrations of total (gas phase and PM_{2.5}) PAHs obtained from Toronto samples.

Compound	Concentration (ng m ⁻³)				
	July 23 rd 2013	Oct. 29 th 2013	Dec. 12 th 2013	Feb. 16 th 2015	Feb. 23 rd 2015
NAP	< DL	< DL	9.1 ± 3.6	65 ± 22	52 ± 18
ACY	0.37 ± 0.04	0.10 ± 0.01	0.36 ± 0.04	0.10 ± 0.01	0.07 ± 0.01
ACE	1.5 ± 0.2	2.4 ± 0.4	1.2 ± 0.2	2.4 ± 0.4	0.9 ± 0.1
FLU	2.4 ± 0.5	2.3 ± 0.5	1.9 ± 0.4	2.8 ± 0.6	1.3 ± 0.3
PHE	3.6 ± 0.8	2.9 ± 0.6	3.4 ± 0.8	3.3 ± 0.7	1.8 ± 0.4
ANT	0.032 ± 0.004	0.08 ± 0.01	0.035 ± 0.004	0.12 ± 0.01	0.026 ± 0.004
FLT	0.50 ± 0.07	0.35 ± 0.05	0.9 ± 0.1	0.8 ± 0.1	0.51 ± 0.07
PYR	0.22 ± 0.03	0.25 ± 0.04	0.60 ± 0.09	0.9 ± 0.1	0.39 ± 0.06
BaA	0.015 ± 0.003	0.05 ± 0.01	0.12 ± 0.02	0.22 ± 0.03	0.12 ± 0.02
CRY	< DL	0.07 ± 0.01	0.24 ± 0.03	0.30 ± 0.03	0.19 ± 0.02
BbF	< DL	0.07 ± 0.01	0.26 ± 0.03	0.29 ± 0.03	0.14 ± 0.02
BkF	< DL	0.025 ± 0.004	0.16 ± 0.02	0.09 ± 0.01	0.06 ± 0.01
BaP	< DL	< DL	0.17 ± 0.02	0.16 ± 0.02	0.02 ± 0.01
IND	< DL	0.030 ± 0.003	0.07 ± 0.01	0.32 ± 0.03	0.18 ± 0.02
dBahA	< DL	< DL	< DL	0.05 ± 0.01	0.023 ± 0.003
BghiP	< DL	0.039 ± 0.004	0.05 ± 0.01	0.33 ± 0.03	0.14 ± 0.01

< DL: concentrations that were less than the detection limit

4.2.3 Gas Phase and PM Concentration Measurements of SVOCs

Gas phase and PM concentrations of nitrophenols, PAHs, and n-alkanes in the atmosphere were obtained from three parallel sampling tests. For each test a XAD-4TM SIF for total (gas phase and PM) collection and an uncoated QFF for PM collection were used to sample ambient air using two separate high volume air samplers. The fractions in the gas phase and in the PM were calculated using Eq. 4.5 and 4.6, respectively. The results for the three classes of SVOCs are shown in Tables 4.21, 4.22 and 4.23.

$$\text{Percent in PM} = \frac{\text{Mass on uncoated QFF}}{\text{Mass on XAD4 SIF}} \times 100 \% \quad \text{Eq. (4.5)}$$

$$\text{Percent in Gas Phase} = \frac{\text{Mass on XAD4 SIF} - \text{Mass on uncoated QFF}}{\text{Mass on XAD4 SIF}} \times 100 \% \quad \text{Eq. (4.6)}$$

Table 4.21: Ambient concentrations of nitrophenols in gas phase and PM_{2.5} from Toronto samples.

Compound	Concentration (ng m ⁻³)					
	Dec. 12 th 2013		Feb. 16 th 2015		Feb. 23 rd 2015	
	Gas + PM	PM	Gas + PM	PM	Gas + PM	PM
4-me-2-NP	2.2 ± 0.2	0.16 ± 0.01	12 ± 1	0.07 ± 0.01	15 ± 1	0.43 ± 0.04
4-NP	17 ± 3	4.4 ± 0.7	18 ± 3	16 ± 2	20 ± 3	14 ± 2
3-me-4-NP	1.85 ± 0.04	0.58 ± 0.01	4.22 ± 0.09	3.20 ± 0.07	4.57 ± 0.09	1.54 ± 0.03
2-me-4-NP	1.63 ± 0.05	0.63 ± 0.02	9.0 ± 0.3	5.7 ± 0.2	6.7 ± 0.2	2.75 ± 0.09
2,6-dime-4-NP	0.432 ± 0.004	0.133 ± 0.001	2.79 ± 0.03	1.23 ± 0.01	0.98 ± 0.01	0.48 ± 0.01

Table 4.22: Ambient concentrations of n-alkanes in gas phase and PM_{2.5} from Toronto samples.

Compound	Concentration (ng m ⁻³)					
	Dec. 12 th 2013		Feb. 16 th 2015		Feb. 23 rd 2015	
	Gas + PM	PM	Gas + PM	PM	Gas + PM	PM
C ₁₃	18 ± 3	< DL	231 ± 41	1.8 ± 0.3	47 ± 8	0.6 ± 0.1
C ₁₄	29 ± 8	< DL	286 ± 78	5 ± 1	67 ± 18	< DL
C ₁₅	15 ± 4	< DL	85 ± 25	2.8 ± 0.8	24 ± 7	< DL
C ₁₆	10 ± 3	< DL	39 ± 10	2.3 ± 0.6	12 ± 3	< DL
C ₁₇	5 ± 1	< DL	11 ± 3	2.6 ± 0.6	4 ± 1	< DL
C ₁₈	2.7 ± 0.8	< DL	6 ± 2	4.4 ± 1.3	1.8 ± 0.6	1.3 ± 0.4
C ₁₉	0.9 ± 0.3	< DL	4 ± 1	2.9 ± 0.8	1.1 ± 0.3	0.9 ± 0.2
C ₂₀	0.6 ± 0.1	< DL	2.9 ± 0.5	2.2 ± 0.4	0.7 ± 0.2	0.54 ± 0.09
C ₂₁	0.6 ± 0.1	0.43 ± 0.05	1.2 ± 0.2	0.9 ± 0.1	0.5 ± 0.1	0.30 ± 0.04
C ₂₂	0.6 ± 0.1	< DL	0.6 ± 0.1	0.4 ± 0.1	< DL	< DL
C ₂₃	0.5 ± 0.1	< DL	< DL	< DL	< DL	< DL
C ₂₄	1.1 ± 0.3	< DL	< DL	< DL	< DL	< DL
C ₂₅	1.6 ± 0.4	0.71 ± 0.05	1.0 ± 0.4	1.0 ± 0.1	0.6 ± 0.3	0.52 ± 0.04

< DL: concentrations that were less than the detection limit.

Table 4.23: Ambient concentrations of PAHs in gas phase and PM_{2.5} from Toronto samples.

Compound	Concentration (ng m ⁻³)					
	Dec. 12 th 2013		Feb. 16 th 2015		Feb. 23 rd 2015	
	Gas + PM	PM	Gas + PM	PM	Gas + PM	PM
NAP	9.1 ± 3.6	< DL	65 ± 22	< DL	52 ± 18	< DL
ACY	0.36 ± 0.04	< DL	0.10 ± 0.01	<DL	0.07 ± 0.01	< DL
ACE	1.2 ± 0.2	< DL	2.4 ± 0.4	< DL	0.9 ± 0.1	< DL
FLU	1.9 ± 0.4	< DL	2.8 ± 0.6	0.26 ± 0.06	1.3 ± 0.3	0.17 ± 0.04
PHE	3.4 ± 0.8	0.20 ± 0.04	3.3 ± 0.7	0.7 ± 0.1	1.8 ± 0.4	0.5 ± 0.1
ANT	0.035 ± 0.004	0.007 ± 0.001	0.12 ± 0.01	0.051 ± 0.005	0.026 ± 0.004	0.014 ± 0.001
FLT	0.9 ± 0.1	0.31 ± 0.04	0.8 ± 0.1	0.70 ± 0.09	0.51 ± 0.07	0.47 ± 0.06
PYR	0.60 ± 0.09	0.19 ± 0.03	0.9 ± 0.1	0.8 ± 0.1	0.39 ± 0.06	0.32 ± 0.05
BaA	0.12 ± 0.02	0.07 ± 0.01	0.22 ± 0.03	0.21 ± 0.03	0.12 ± 0.02	0.11 ± 0.02
CRY	0.24 ± 0.03	0.17 ± 0.02	0.30 ± 0.03	0.28 ± 0.03	0.19 ± 0.02	0.19 ± 0.02
BbF	0.26 ± 0.03	0.14 ± 0.02	0.29 ± 0.03	0.28 ± 0.03	0.14 ± 0.02	0.14 ± 0.02
BkF	0.16 ± 0.02	0.084 ± 0.007	0.09 ± 0.01	0.091 ± 0.008	0.06 ± 0.01	0.055 ± 0.005
BaP	0.17 ± 0.02	0.15 ± 0.02	0.16 ± 0.02	0.15 ± 0.02	0.02 ± 0.01	0.015 ± 0.002
IND	0.07 ± 0.01	0.043 ± 0.004	0.32 ± 0.03	0.28 ± 0.03	0.18 ± 0.02	0.17 ± 0.02
dBahA	< DL	< DL	0.05 ± 0.01	0.048 ± 0.005	0.023 ± 0.003	0.020 ± 0.002
BghiP	0.05 ± 0.01	0.029 ± 0.003	0.33 ± 0.03	0.32 ± 0.03	0.14 ± 0.01	0.13 ± 0.01

< DL: concentrations that were less than the detection limit.

5 Discussion

This chapter begins with a discussion of the overall performance of the modified method used in this project. The results obtained from various tests performed to validate the suitability of the XAD-4TM SIF analytical method for analyzing PAH and n-alkanes will then be explained. The chapter concludes with a discussion of the results obtained from ambient samples from both Toronto and Oil Sands using the modified method.

5.1 Method Evaluation

5.1.1 Blank Values and Detection Limits

The detection limits found for the three classes of SVOCs in this project were mainly influenced by the blank values present on QFF and XAD-4TM resin itself. Although QFFs were baked prior to use in order to remove organic contaminants, their blank values may have been impacted by storage before coating due to their tendency to adsorb organic hydrocarbon gases (Chow, 1995). Moreover, XAD resin is known to contain organic impurities such as NAP, PHE and a series of hydrocarbons (C₈ to C₂₄), which are supposed to be trapped by the resin during the manufacturing process (Junk et al., 1974; James et al., 1981; Hunt and Pangaro, 1982; Lane and Gundle, 1995). It is hypothesized that the trapped organic impurities are released upon the resin bead rapture, which then expose new surfaces which can impact the blank value of the XAD resin (Junk et al., 1974; Daignault et al., 1988). Figures 5.1 and 5.2 illustrate the ratio of blank mass found on QFF to the average blank mass obtained from XAD-4TM SIFs for target PAHs and n-alkanes, respectively.

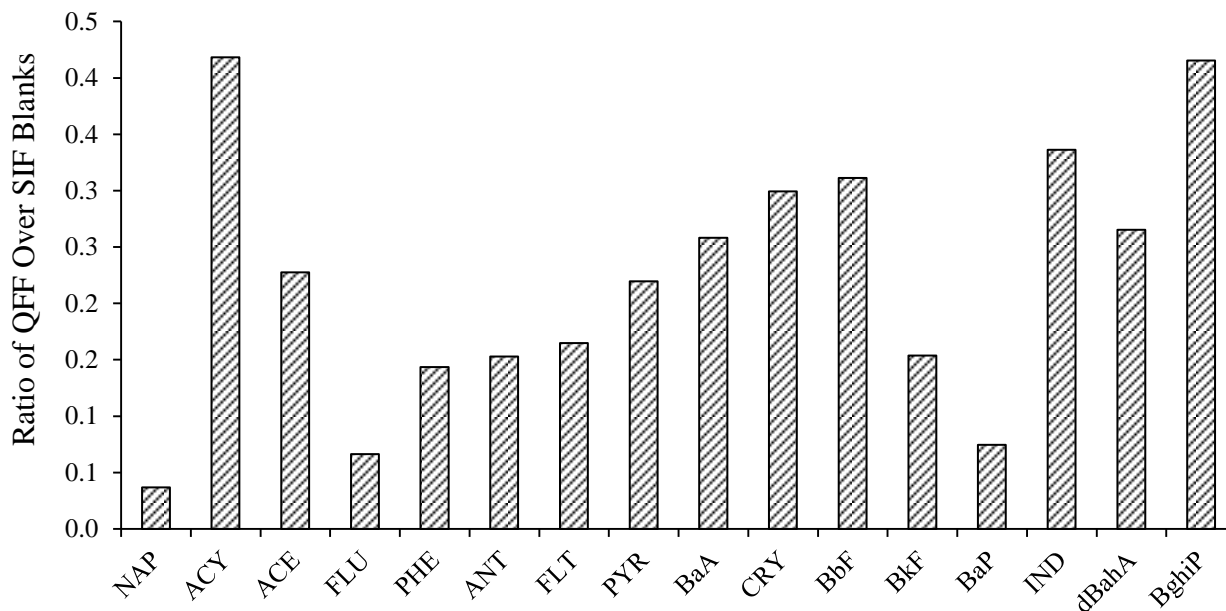


Figure 5.1: The ratio of QFF blank mass to the average blank mass found on XAD-4TM SIFs for target PAHs.

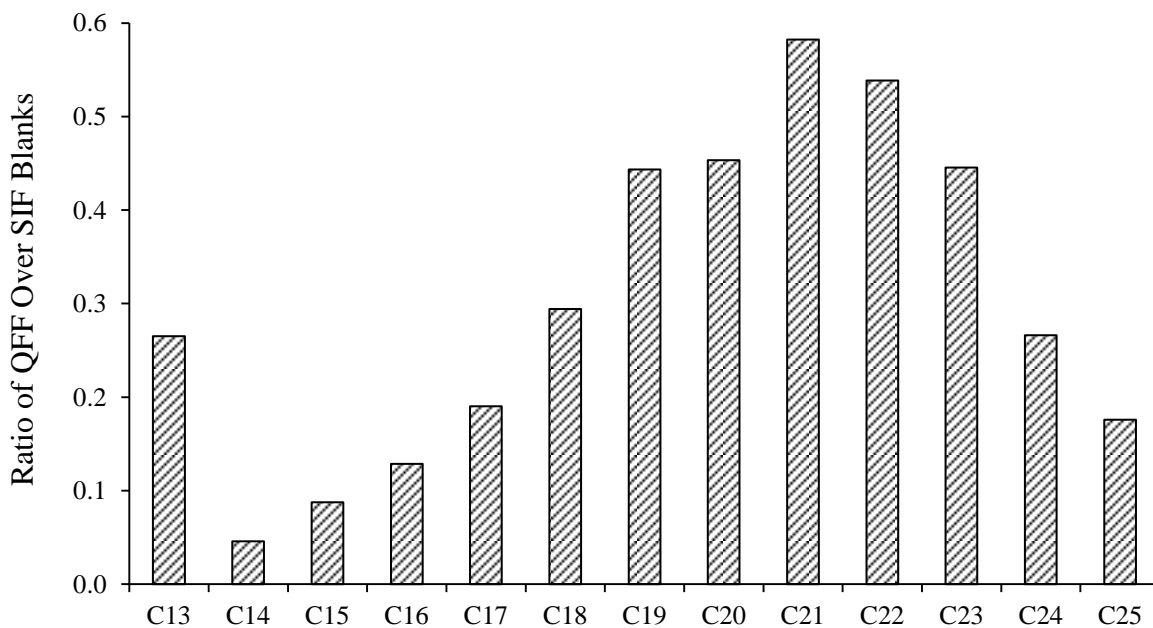


Figure 5.2: The ratio of QFF blank mass to the average blank mass found on XAD-4TM SIFs for target n-alkanes.

From the results it can be seen that for most target compounds the blank contribution from the QFF is less than 30 %. This indicates that the main contribution to the blank values observed in this project was from organic impurities that, as mentioned above, are present on the XAD adsorbent. The blank values for XAD-4TM SIF were found to be in the pg m⁻³ range for most target PAHs and nitrophenols and in the sub ng m⁻³ range for n-alkanes (Tables 4.1, 4.2, and 4.3). Significantly higher blank values, however, were observed for low molecular mass n-alkanes (C₁₄ to C₁₉), 4-nitrophenol, and several PAHs (NAP, ACE, FLU and PHE). n-Alkanes are least impacted by the blank values since the ambient concentration range expected for these compounds is much higher than the blank values observed (Table 2.4). For 4-nitrophenol, high blank values on both XAD-4TM SIF and uncoated QFF were also reported by research carried out earlier by Dr. Rudolph's group (Facca, 2013; Saccon, 2013). However, this compound is found to have the highest ambient concentration of the five target nitrophenols (Table 2.6) and therefore is not significantly impacted by the blank value. In the case of the target PAHs, other studies have also reported high blank value for PHE on both PUF and QFF (Odabasi et al., 1999; Demircioglu et al., 2011). Nevertheless, PHE is the most abundant of the target PAHs in the atmosphere (Table 2.5) hence this compound is least affected by the blank value. Figures 5.3 and 5.4 show the ambient detection limits for the target PAHs compared to high and low ambient concentrations of PAHs from Toronto and Oil Sands samples, respectively.

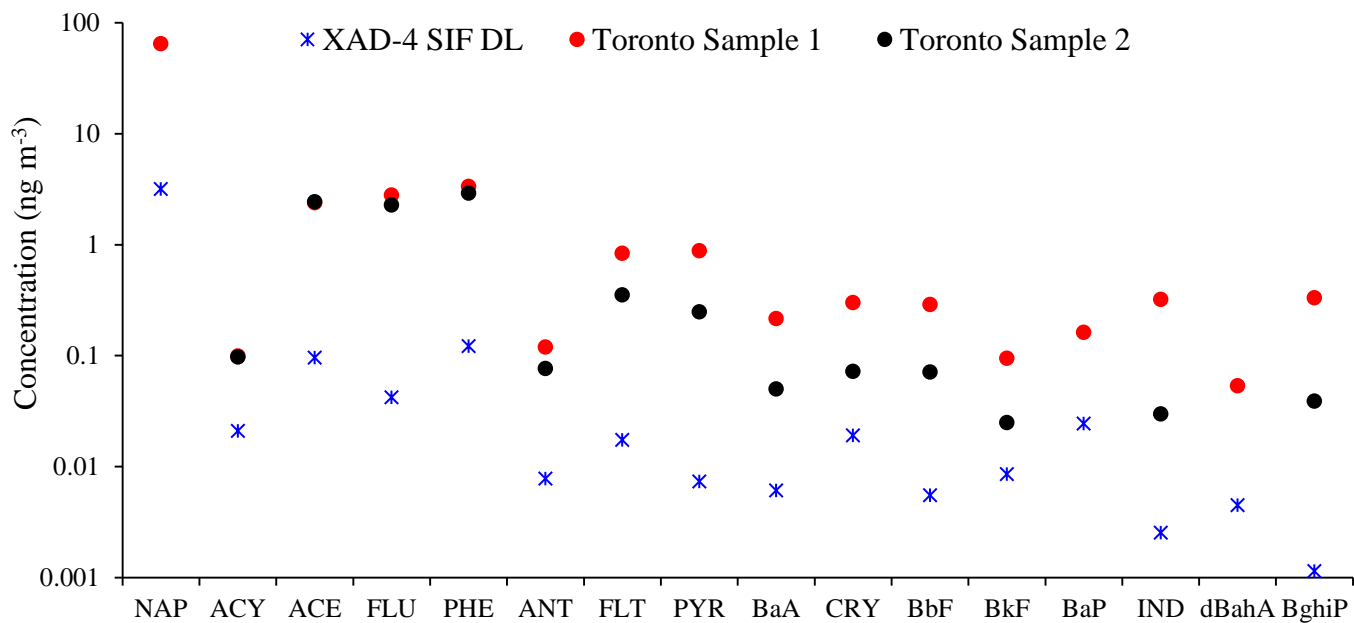


Figure 5.3: Comparison of the ambient detection limits (DL) of target PAHs with high (sample 1) and low (sample 2) ambient concentrations of PAHs obtained from two Toronto samples.

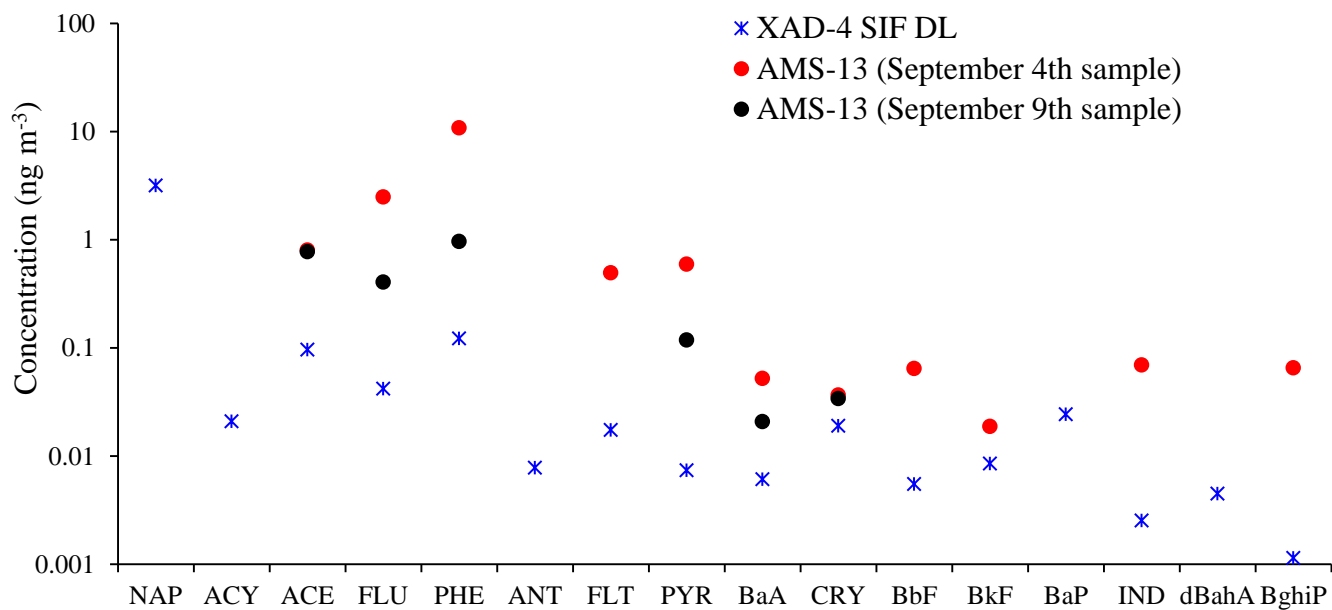


Figure 5.4: Comparison of the ambient detection limits (DL) of target PAHs with high (September 4th) and low (September 9th) ambient concentrations of PAHs obtained from two Oil Sands samples.

From the results it can be seen that the ambient detection limits for most PAHs observed in this research, apart from NAP, are low enough to monitor their concentrations on both Toronto and Oil Sands samples even for the samples with low ambient concentrations. The result observed for NAP was expected due to relatively higher blank value associated with this compound.

In order to determine if there were significant blank value contributions from the transportation of XAD-4TM SIF to and from the Oil Sands sampling site, two field blanks were acquired. The blank values obtained from the field SIFs were not significantly different (within 10%) from the other SIF blanks for both PAHs and n-alkanes. In the case of nitrophenols, however, a relatively higher blank value was observed for 4-me-2-NP, which may be due to the interference of a contaminant that occurred during transportation or while collecting samples during the field campaign.

5.1.2 Linearity and Measurement Precision

The linear regression (R^2) values obtained from the GC-MS calibration curves for each target compound were between 0.97 and 1. The calibration curves were forced through the origin and the relative contribution from uncertainties in calibration curves to the overall uncertainties of the measurements was obtained from the relative standard deviations of the slopes. The error of the slope for PAHs was 10 % or lower and 5 % or lower for target n-alkanes and nitrophenols. The intercepts for the calibration curves were set to zero due to statistically insignificant axis intercepts. The percent difference in the slope either including or excluding the intercept was within 10 %.

The reproducibility for concentration measurements in this work was determined by using data obtained from the GG-MS measurements that were run twice (Tables 4.6 and 4.7). The average uncertainty of the repeat measurements for nitrophenols was determined to be 6 %. The uncertainty detected for most target PAHs was 10 % or lower and between 20 % and 33 % for several low molecular mass PAHs (NAP, ACE, FLU and PHE). For the target n-alkanes, the uncertainty for the heavier compounds (C₂₀ to C₂₅) was found to be lower than 20 % and between 20 % and 30 % for the lighter n-alkanes (C₁₄ to C₁₉). The relatively larger error obtained for the lower molecular mass PAHs and n-alkanes may be due to loss of these volatile compounds during GC injections. However, this needs to be investigated in more detail in future.

5.2 Method Validation Tests

5.2.1 Internal Standard Selection and Recoveries

The internal standards selected for analysis of the target PAHs were naphthalene-D₈, acenaphthene-D₁₀, phenanthrene-D₁₀, and chrysene-D₁₂. Two internal standards, C₁₂D₂₆ and C₁₉D₄₀, were originally selected for analysis of n-alkanes. However, the recovery of C₁₂D₂₆ compared to C₁₉D₄₀ and relative to its spiked mass was consistently low and this was thought to be a consequence of the high volatility of C₁₂D₂₆. Therefore C₁₉D₄₀ was used as the internal standard for all target n-alkanes. The deuterated version of the target PAHs and n-alkanes was selected since they behave similarly to the target compounds and are not found in significant amounts in the atmosphere.

The recoveries of the internal standards were not used to calculate the ambient concentration of the target compounds; they were mainly used as a diagnostic tool for the extraction and analysis procedure. The ambient concentrations were calculated by directly comparing the peak areas of the target compound and its respective internal standard, as was explained in section 3.3.6. As such, the uncertainty in the measurements resulting from the changes in the instrumental sensitivity is eliminated.

The average recoveries obtained for PAHs (Table 4.8) from spiked XAD-4TM SIFs were between 43 % and 69 %. The low recoveries were expected due the extensive extraction procedure, which often results in the loss of the target compounds. The extraction efficiency of NAP remains uncertain due to the large blank value associated with this compound. For most of the target n-alkanes (Table 4.9), the average recoveries were between 45 % and 77 %. Exceptions were for lighter (C₁₃ to C₁₅) and heavier (C₂₄ to C₂₅) n-alkanes, which had recoveries lower than 45 %. A possible explanation for the low recoveries of the lighter n-alkanes may be the relatively higher vapour pressure associated with these compounds. In the case of the heavier n-alkanes, the low recoveries may be due to the high adsorptive characteristic of XAD-4TM resin, which could have resulted in the stronger retention and thus incomplete extraction of these compounds. Generally, the larger the molecule, the stronger it is retained by the XAD-4TM resin.

The ratios of the recoveries relative to the internal standard are expected to be one if the internal standard has the same physical and chemical properties as the target compound. For most PAHs, the ratio was generally close to one, within the standard deviation of the measurements (Table 4.8). This indicates that the internal standards selected for the target PAH compounds was appropriate. The recoveries relative to the

internal standards for the lighter and heavier n-alkanes were significantly lower than one. This is not surprising since only one useful deuterated n-alkane ($C_{19}D_{40}$) was used and the vapour pressure and adsorption properties of n-alkanes depend on carbon number. Therefore, the recovery ratios obtained for the lighter and heavier n-alkanes were used to correct the ambient concentrations of these compounds.

There was concern that some of the target SVOCs may have been lost when they were taken out of their freezer storage during transportation from the Oil Sands. This is because the samples were stored in a cooler filled with ice packs while being transported. However, the trip took roughly five days and ice packs generally remain frozen for only 24 to 36 hours. In order to determine if losses due to storage occurred, two XAD-4TM SIFs that were spiked with target compounds and stored at room temperature for five days before extraction were compared to those that were extracted immediately after spiking. The results are shown in Figures 5.5, 5.6 and 5.7. Comparison between the two recoveries suggests no significant loss occurred due to room temperature storage for PAHs and most target nitrophenols, except for 2,6-dimethy-4-nitrophenol. In the case of n-alkanes, however, significant loss was observed for the lower molecular mass compounds, which was expected considering their relatively higher vapour pressures. Consequently, the ambient concentrations for the low molecular mass n-alkanes obtained from the Oil Sands samples are the lower limits.

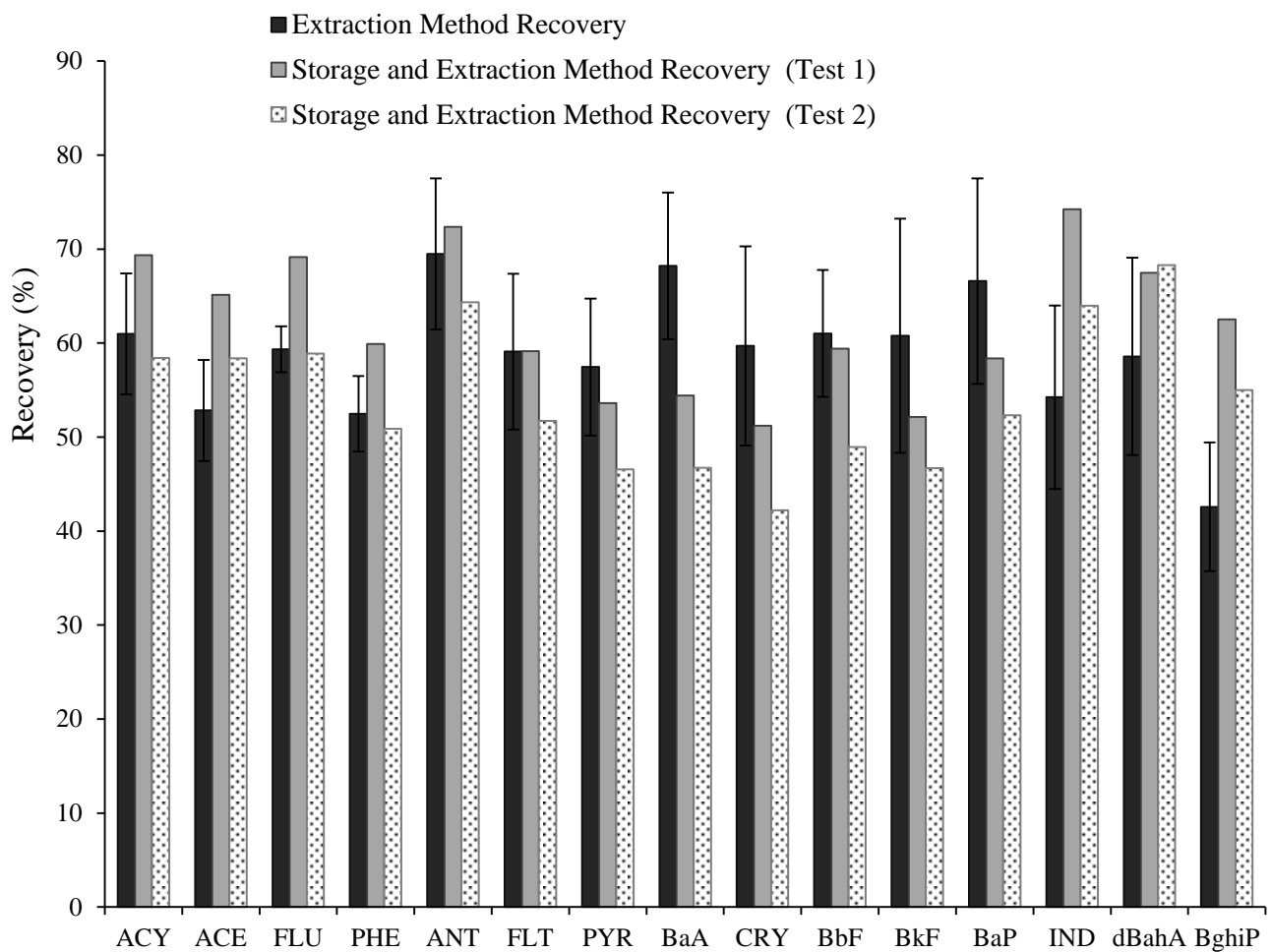


Figure 5.5: Comparison of the target PAHs recoveries from blank XAD-4TM SIFs that were spiked, stored at room temperature for five days and analyzed with the average recoveries from the filters that were spiked and analyzed without storage. The error bar represents the standard deviation of the measurements.

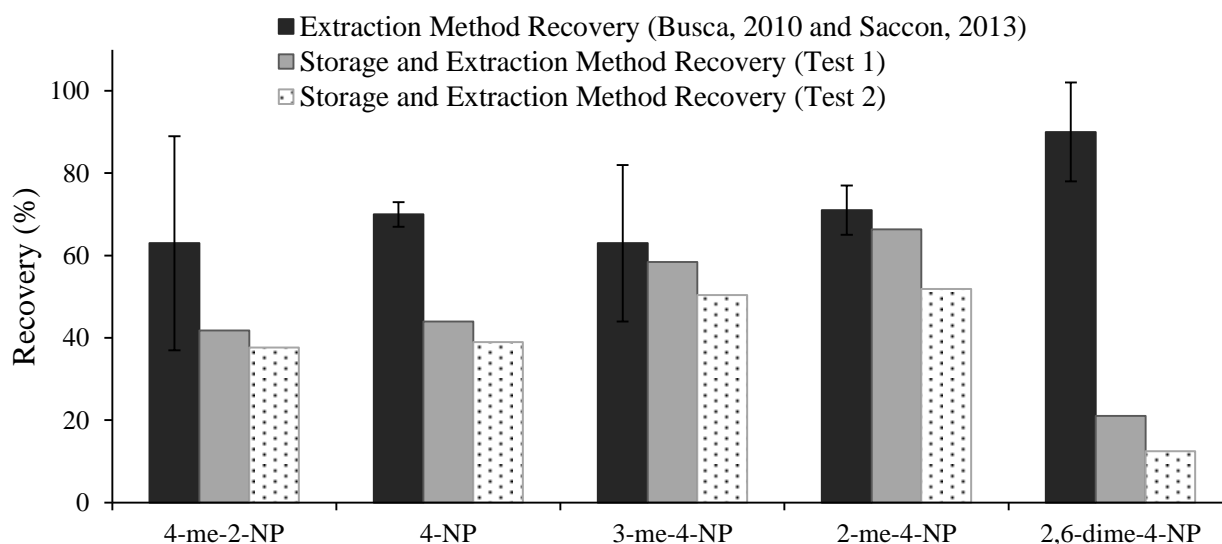


Figure 5.6: Comparison of the target nitrophenols recoveries from blank XAD-4TM SIFs that were spiked, stored at room temperature for five days and analyzed with the average recoveries from the filters that were spiked and analyzed without storage reported by Busca (2010) and Saccon (2013). The error bar represents the standard deviation of the measurements.

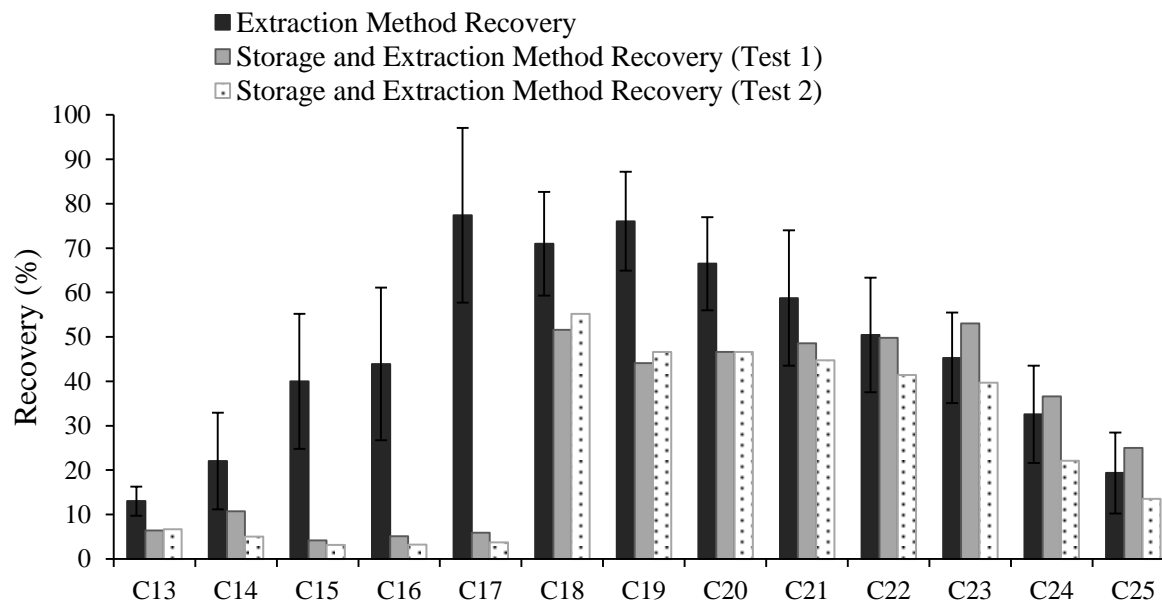


Figure 5.7: Comparison of the recoveries from blank XAD-4TM SIFs that were spiked, stored at room temperature for five days and analyzed with the average recoveries from the filters that were spiked and analyzed without storage. The error bar represents the standard deviation of the measurements.

5.2.2 XAD-4TM SIF Sampling Efficiency

To test the efficiency of XAD-4TM SIF for PAH and n-alkanes sampling, two filters were sampled in series. With this sampling configuration, the bottom filter will capture breakthrough from the top filter. From the results shown in Tables 4.12 and 4.13, it can be seen that the percentage of both PAHs and n-alkanes found on the top filter were generally greater than 80 % of the total collected on both filters. Moreover, the greater breakthrough was mainly observed for the lower molecular mass and more volatile compounds, as expected. Galarneau et al. (2006) also reported approximately 80 % collection efficiency for XAD-4TM SIF in a study aimed at assessing the XAD-4TM SIF as an alternative method to PUF for sampling gas phase SVOCs, including several PAH compounds.

5.2.3 Parallel Sampling Reproducibility

Parallel sampling was used in this research for phase partitioning measurements of the selected classes of SVOCs. This technique involves collection of ambient samples on two separate filters using two separate high volume air samplers that are run simultaneously under the same conditions. Since only one of the two air samplers was calibrated directly, there were some concerns regarding the validity of the parallel sampling using these two high volume air samplers. In order to investigate the reproducibility of parallel sampling using the two air samplers, a test was performed where three QFFs were run in parallel using three separate high volume air samplers (the slotted impactor high volume air sampler was used as the third sampler), two of which

were calibrated directly prior to sampling. Table 4.14 shows that the ambient concentrations obtained for the target nitrophenols, from each high volume samplers, exhibit good reproducibility with an error of less than 20 % for most compounds. This therefore validates the reproducibility of parallel sampling using the two PM high volume air samplers.

5.2.4 Sampling Target SVOCs in PM 2.5

Most of the ambient samples collected in Toronto in this study used high volume air samplers equipped with PM_{2.5} heads, which collected particles that were 2.5 µm and smaller. Unlike nitrophenols, the particle size distribution of PAHs and n-alkanes in the atmosphere has been studied and characterized by many research groups (Kadowaki et al., 1994; Kiss et al., 1998; Bi et al., 2005; Li et al., 2013; Ladji et al., 2014). According to these studies, PAHs and n-alkanes are mainly associated with PM_{2.5} and smaller. To examine the extent to which nitrophenols are found in PM larger than 2.5 µm, ambient samples were collected using a slotted impactor high volume air sampler since it allows simultaneous collection of both PM > 2.5 µm and PM ≤ 2.5 µm. The results (Table 4.15) demonstrated that the majority of the target nitrophenols exist in PM_{2.5} and smaller, because less than 5 % of each target nitrophenol was found in PM larger than 2.5 µm. Saccon (2013) also reported negligible amounts (pg m⁻³) of nitrophenols in PM larger than 2.5 µm in an experiment where QFFs were sampled in parallel, with one sampler collecting PM_{2.5} and the other collecting PM₁₀. These results are in agreement with the

theory that secondary organic compounds are mainly found in the particle size range of 2.5 μm and smaller (Finlayson-Pitts and Pitts, 2000).

5.3 Ambient SVOCs Measurements from Oil Sands

The modified extraction and analysis procedures were used to analyze the ambient samples that were collected during the summer 2013 Oil Sands field campaign at AMS-13. The seven Oil Sands samples analyzed in this work were collected between September 1st and September 9th 2013. The jar containing the filter sample from September 7th was broken during transportation from the Oil Sands field campaign and this may have resulted in the sample being contamination and/or loss of some target compounds. For this reason, the ambient concentrations of n-alkanes, PAHs, and nitrophenols obtained for this particular sample were not used as part of the analysis of the Oil Sands samples. Some of the samples collected during this field campaign coincided with plume events from upgrading facilities that were located in the vicinity of AMS-13. Table 5.1 presents preliminary characterization of the sampling condition observed for each sample collected during the Oil Sands field campaign. The average daily wind direction for each sampling event at AMS-13 reported by Dr. Strawbridge (private communication) was also determined. The average daily wind direction was generally found to originate from the south and southwest, where there are possible impacts from two upgrading facilities (namely, Syncrude and Suncor), several tailing-ponds and open pit mines.

Table 5.1: Preliminary sampling conditions observed during Oil Sands field campaign.

Sampling Date	Sampling Time (hours)	Sampling Condition ^(a)
Sept. 1 st	19	Relatively clean day
Sept. 2 nd	26	Plume observed morning of Sept. 3 rd
Sept. 4 th	7	Heavy plume observed during sampling
Sept. 6 th	24	Plume observed morning of Sept. 7 th
Sept. 7 th	24	Heavy plume observed during sampling
Sept. 8 th	23	Clear day, no plume observed
Sept. 9 th	10	Clear day, no plume observed

^(a) Preliminary sampling condition was provided by Dr. McLaren's group (private communication).

5.3.1 n-Alkanes

The ambient concentration results for n-alkanes are summarized in Table 4.17 and are shown in Figure 5.8. From these results, it can be seen that the concentrations for the lighter n-alkanes (C_{14} to C_{19}) for the samples collected on September 1st, 2nd and 6th were generally higher compared to the samples from September 8th and 9th. Significantly higher concentrations, however, were noticed for the sample from September 4th. These findings are in agreement with sampling conditions observed for these samples. For example, the plume from nearby upgrading and refining facilities significantly impacted the sample from September 4th and all other samples but the ones from September 8th and 9th were lightly influenced by the plume events from the nearby upgrading facilities. The concentration levels for several low molecular mass n-alkanes obtained from September 4th sample were similar to the concentration levels found in Toronto (Table 4.20), which, unlike the Oil Sands region, is an urban area with a higher and denser population. Furthermore, the concentration levels obtained from September 8th and 9th samples were

not significantly different from the samples lightly impacted by the plume from nearby upgrading facilities. This therefore implies anthropogenic impact from other sources.

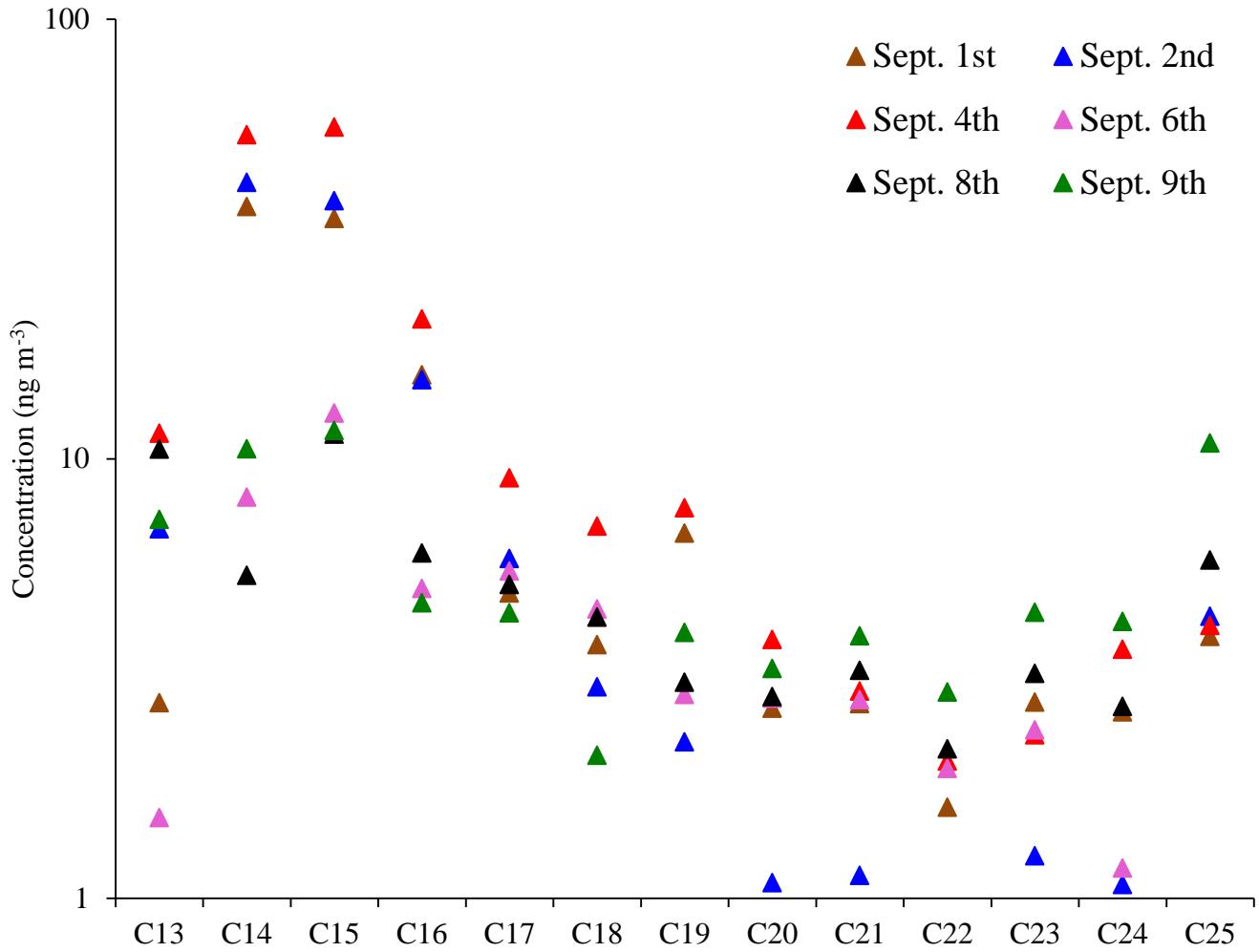


Figure 5.8: Ambient concentrations of n-alkanes from six Oil Sands samples.

In order to determine the impact from anthropogenic and biogenic emission sources, the CPI value was calculated for each sampling event. The CPI value obtained for each Oil Sands sample was in the range of 0.93 to 1.80, which is in agreement with

the petroleum-dominated input with CPI values of 1 to 3 (Eichmann et al., 1979; Mazurek et al., 1989). Moreover, the carbon distribution plots (Figure 5.9) show a relatively smooth pattern for samples impacted by a plume, which is consistent with the n-alkane distribution pattern observed by Simoneit et al. (1984) for the petroleum related emissions (Figure 2.1 a). On the other hand, the samples from September 8th and 9th showed a saw-tooth distribution pattern, which is characteristic of biogenic emissions. However, the CPI value of 1.67 and 1.80 observed for these samples suggests that the emissions are not entirely biogenic and may have been impacted by other Oil Sands related activities or possibly even emissions from biomass burning.

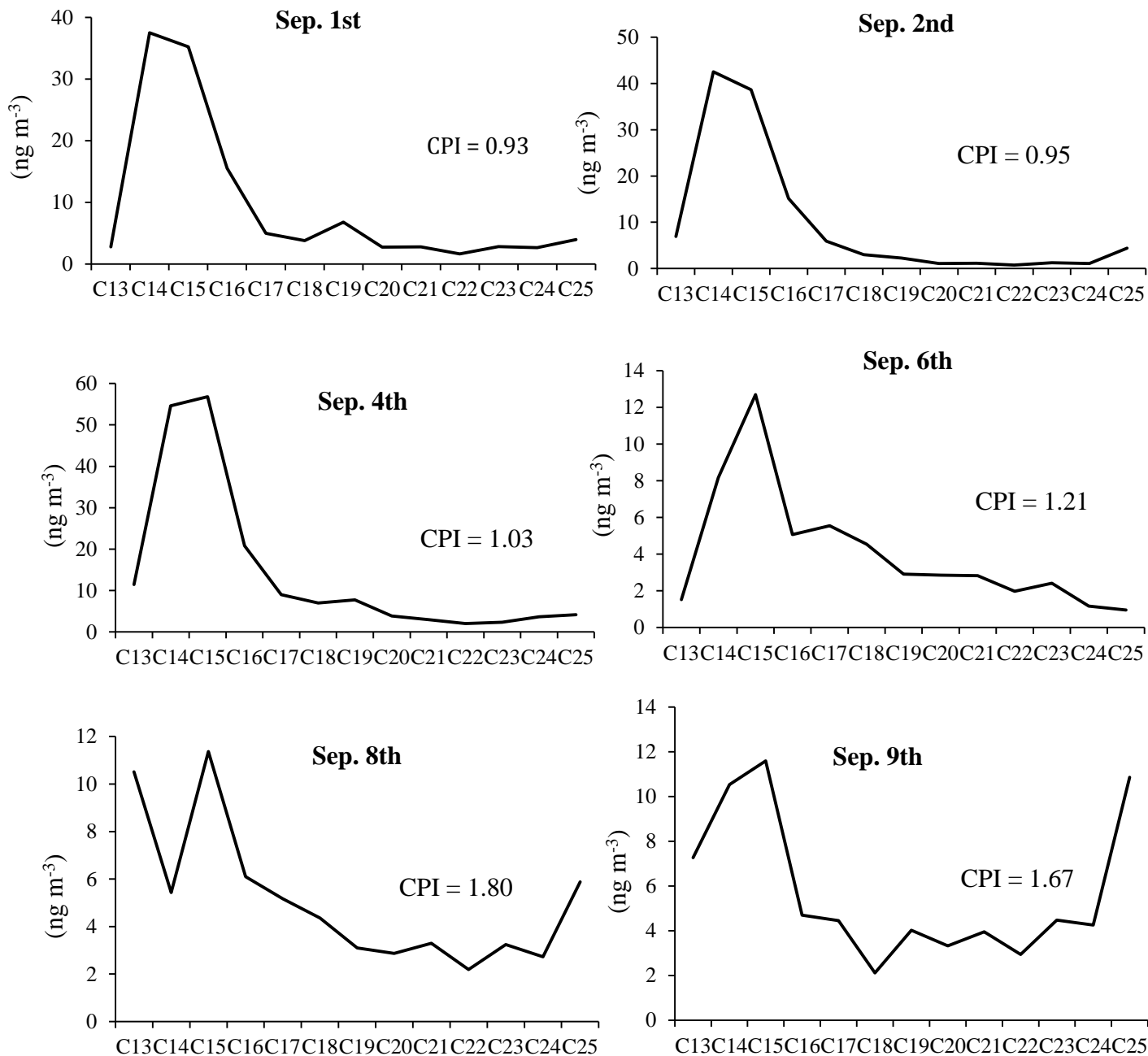


Figure 5.9: n-Alkane concentrations as function of carbon number for Oil Sands samples.

5.3.2 PAHs

The impact of the Oil Sands development on the environmental concentration levels of PAHs has been investigated by a few published studies. For example, Kelly et al. (2009) suggest that Oil Sands mining and processing has been contributing significant amounts of PAHs to the Athabasca River. In a study on sediment cores from lakes in the Athabasca, Kurek et al. (2013) show how there is a significant increase in PAH levels with increasing Oil Sands developments from 1960 to the present. Parajulee and Wania (2014) and Galarneau et al. (2014) have suggested possible PAHs emissions from tailing-ponds. A very recent study by Hsu et al. (2015) measured the ambient concentration of PAHs in four air-monitoring stations (AMS) in the Alberta Oil Sands region. According to this study, the major sources of PAHs in this region are emissions from industrial stacks, fugitive emissions from surface mining and emission from heavy hauler mine fleets.

The ambient concentration levels of PAHs for the Oil Sands samples observed in this study are summarized in Table 4.21. These results show that the highest concentrations were dominated by the low molecular mass PAHs including ACE, FLU, PHE, FLT, and PYR. Moreover, the concentration levels for most target PAHs were relatively higher for the samples from September 1st, 2nd, 4th and 6th compared to the samples from September 8th and 9th. This again is consistent with the results found for n-alkanes and the preliminary sampling conditions observed for these days (Table 5.1). Like n-alkanes, the concentration levels of PAHs for the samples from September 8th and 9th were found not to be significantly different from the samples that have been lightly impacted by the plume from nearby upgrading facilities. However, unlike n-alkanes,

PAHs do not have biogenic emission sources. Therefore, the fact that PAHs are found in detectable amounts even for the samples not influenced by the industrial stack emissions indicates that there are other anthropogenic sources that contribute to PAHs emission in this region. This finding is also in agreement with the low CPI values obtained for the n-alkanes for the same samples. Figure 5.10 presents the PAH concentration levels from September 4th compared to the average PAH concentration levels obtained by Hsu et al. (2015) from three sites in the Oil Sands region as well as the average concentration levels detected in Toronto samples in the present study.

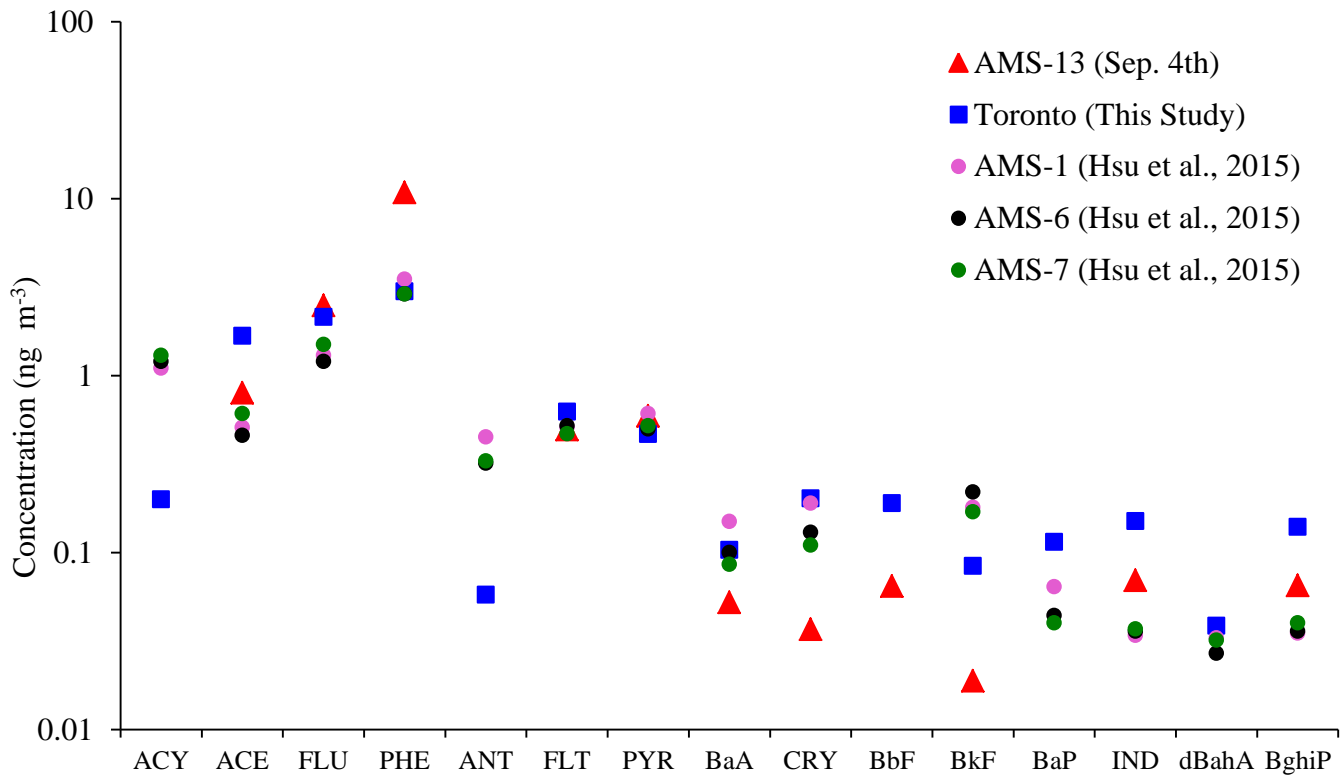


Figure 5.10: Ambient concentrations of target PAHs obtained from September 4th sample from AMS-13 compared to the PAH levels obtained in three sites in the Oil Sands region reported by Hsu et al. (2015) as well as the average PAH levels obtained from Toronto samples in this study.

By comparing the results it can be seen that apart from PHE, the concentration levels for most PAHs obtained from AMS-13 in this study are similar to those reported by Hsu et al. (2015). Moreover, comparison between the PAH levels from the Oil Sands region, found in both this study and those reported by Hsu et al. (2015), show a similar pattern to the levels found in Toronto, even though Toronto is a much larger city with a higher population than Fort McMurray. Furthermore, PHE concentration from AMS-13 was found to be significantly higher compared to the three AMSs reported by Hsu et al. (2015) and the levels found in the Toronto samples. The relatively higher concentration of PHE may be due to an emission source in the vicinity of AMS-13 in the Oil Sands region.

5.3.3 Nitrophenols

Table 4.19 presents the ambient concentrations of nitrophenols obtained from the Oil Sands samples. Similar to what was observed for PAHs and n-alkanes, the concentration levels for the target nitrophenols were found to be relatively higher for the samples from September 1st, 2nd, 6th and especially September 4th compared to the samples from September 8th and 9th. The highest nitrophenol concentration levels were observed for the sample from September 4th and the values from this day are compared to the nitrophenol levels found in Toronto from the samples analyzed in this study and to those acquired by Saccon (2013) in Figure 5.11.

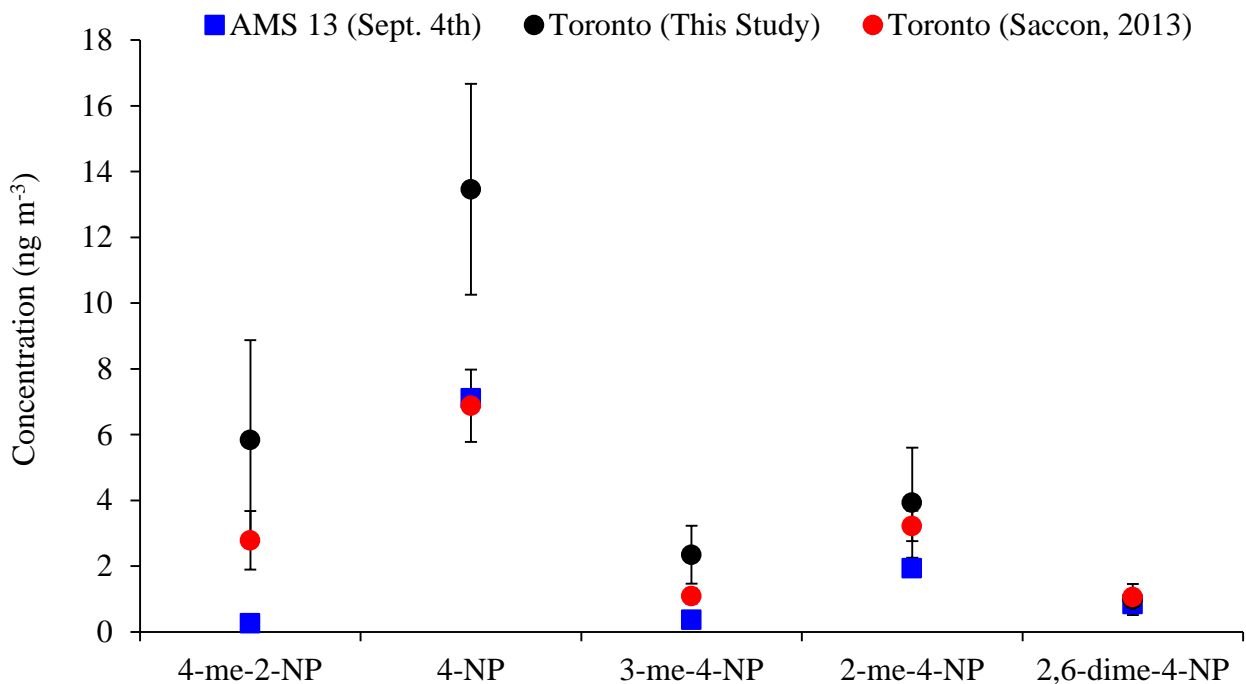


Figure 5.11: Ambient concentrations of nitrophenols from an AMS-13 sample (September 4th) compared to the average nitrophenol concentrations from Toronto samples obtained in this study and to those acquired by Saccon (2013). The error bars represent the error of the mean.

By comparing the concentration levels of nitrophenols from Oil Sands to Toronto samples, similar concentrations were observed. This indicates that the nitrophenols detected at the Oil Sands region may be formed from the same precursors as in Toronto. According to a study by Simpson et al. (2010), nitrophenol precursor levels, such as toluene (401 pptv), benzene (82 pptv) and xylenes (127 to 272 pptv) were found to be higher than the background in the Oil Sands region. The mixing ratios of nitrophenol precursors for each sampling event at AMS-13, obtained by Wang (Government of Canada and Government of Alberta, 2013) are shown in Figure 5.12.

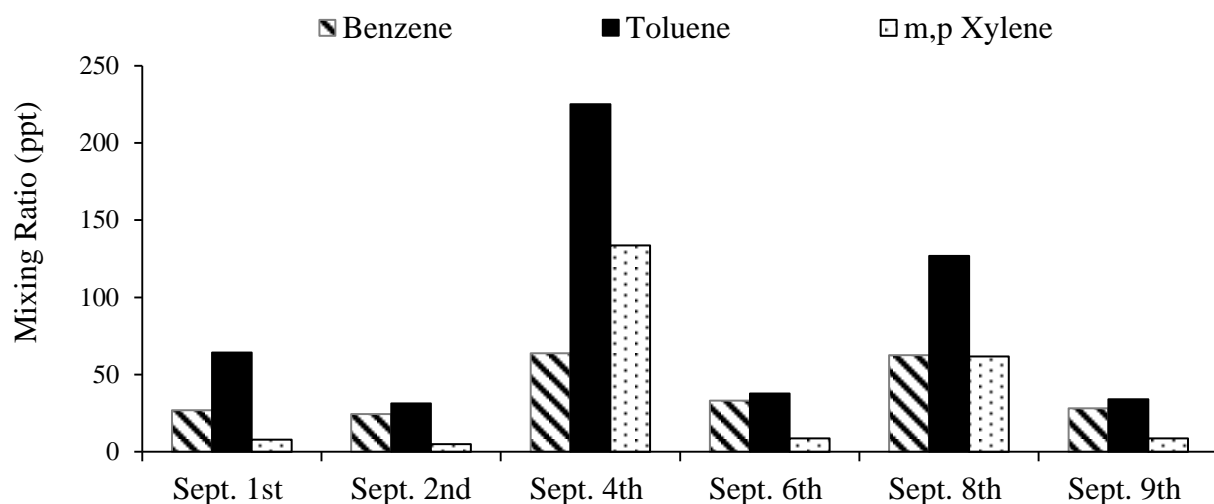


Figure 5.12: Mixing ratios of nitrophenol precursors for different sampling day at AMS-13 (Government of Canada and Government of Alberta, 2013).

By comparing the mixing ratio of nitrophenol precursors from each sampling date, it can be seen that they are indeed higher on September 4th, which is in agreement with the high nitrophenol concentration levels observed on this day. However, the concentration levels of 4-nitrophenol and some methyl nitrophenols were found to be similar to the levels detected in Toronto, despite the relatively lower mixing ratio of their precursors in the Oil Sands region. This result could be due to two reasons. The first could be that these compounds are emitted from primary sources in the Oil Sands region. Although nitrophenols are formed in the atmosphere through photo-oxidization of aromatic VOCs, primary emission sources have been reported for 4-nitrophenol and some methyl nitrophenols in the literature (Nojima et al., 1983; Tremp et al., 1993; Inomata et al., 2013, 2015). Also, it should be noted that the Oil Sands samples were collected during summer where the atmospheric processing can be higher. Therefore, differences in processing may have a different impact on the relationship between precursor and product. This indicates that even though the precursor levels were relatively lower in the

Oil Sands compared to Toronto, the precursors from Oil Sands could have undergone more processing and resulted in more products. The mixing ratio of nitrophenol precursors on September 8th, which unlike September 4th was not impacted by the plume from nearby upgrading facilities (Table 5.1), was also noticed to be relatively higher. This further confirms the results from PAHs and n-alkanes that indicated an anthropogenic impact on this day, possibly from other Oil Sands related activities.

5.3.4 SVOC Correlation with Other Pollutants in the Oil Sands

Major sources of both SO₂ and NO₂ in the Oil Sands region are suggested to be from the upgrading and energy production in the Suncor and Syncrude mining sites (Kindzieerski and Ranganathan, 2006). Heavy hauler mine fleets are also suggested to be a major NO₂ contributor to the atmosphere in this region (Simpson et al., 2010; Hsu et al., 2015). CO is an urban/industrial combustion tracer that can also be emitted from both industrial stacks and other Oil Sands related activities. Aromatic VOCs such as benzene, toluene and xylenes are suggested to be emitted from Oil Sands upgrading as well as direct emission from the diluent used in the Oil Sands extraction processes (Siddique et al., 2006; Simpson et al., 2010). The concentration dependence of the target PAHs, nitrophenols, and n-alkanes on the mixing ratios of pollutants such as SO₂, NO₂, CO, CO₂, CH₄ (Dr. McLaren's group, private communication) and the aromatic VOCs (Government of Canada and Government of Alberta, 2013) – collected during the same field campaign were studied in order to determine potential sources of these SVOCs in the Oil Sands region. The correlation coefficients obtained for each class of SVOCs are summarized in Table 5.2.

Table 5.2: Correlation coefficient (R^2) for nitrophenols, PAHs and n-alkanes with other pollutants measured during the summer 2013 Oil Sands field campaign at AMS-13. For all target compounds it was found that $R^2 \leq 0.38$ with CO_2 and are not included.

Compound	Correlation Coefficient (R^2)						
	SO_2	NO_2	CO	CH_4	Benzene	Toluene	p,m-Xylene
4-me-2-NP	0.57	NS	NS	NS	NS	NS	NS
4-NP	0.84	0.53	0.58	NS	0.52	0.83	0.88
3-me-4-NP	0.85	0.54	0.54	NS	0.44	0.76	0.81
2-me-4-NP	0.88	0.61	0.56	NS	0.43	0.74	0.81
2,6-dime-4-NP	0.90	0.52	NS	NS	NS	0.72	0.78
FLU	0.85	0.44	NS	NS	0.38	0.77	0.79
PHE	0.80	0.42	0.52	NS	0.45	0.82	0.85
FLT	0.66	0.54	0.76	0.48	0.62	0.93	0.94
PYR	0.67	0.43	0.66	NS	0.56	0.88	0.89
BaA	NS	0.36	0.46	0.69	0.46	NS	NS
C_{14}	0.45	NS	NS	NS	NS	NS	NS
C_{15}	0.57	NS	NS	NS	NS	NS	NS
C_{16}	0.44	NS	NS	NS	NS	NS	NS
C_{17}	0.95	0.59	NS	NS	0.35	0.68	0.73
C_{18}	0.63	0.72	NS	NS	0.58	0.77	0.75

NS: Not significant.

From the results, a strong correlation was observed between SO_2 and all target nitrophenols. Most nitrophenols also showed a moderate linear dependence with NO_2 and with CO but no significant dependence was noticed with CH_4 and CO_2 . Moreover, nitrophenols showed strong dependence with both toluene and p,m-xylene but only a weak dependence was noticed with benzene. A possible explanation for the strong correlation observed between SO_2 and nitrophenols may be that nitrophenols or their precursors are emitted from the same source or co-located sources as SO_2 . The correlation noticed for nitrophenols with NO_2 and aromatic VOCs were expected since they are suspected precursor for nitrophenol formation in the atmosphere (Forstner et al., 1997). The weak correlation with benzene may be explained by the lower reactivity of this nitrophenol precursor compared to toluene and p,m-xylene. However, if nitrophenols are emitted from primary sources, their concentration should also be correlated with NO_2 and the aromatic VOCs if they are emitted from the same or co-located sources. Furthermore, nitrophenol concentrations also correlated very well with each other (Figure 5.13). Each target nitrophenol was plotted against 2-me-4-NP and the correlation coefficients obtained were in the range of 0.86 to 0.99, 0.69 to 0.98 and 0.75 to 0.99 with 3-me-4-NP, 4-NP and 2,6-dime-4-NP, respectively. This supports the hypothesis that nitrophenols are formed in the atmosphere by similar processes. However, again, if nitrophenols are emitted from the same or co-located primary sources their concentrations should also be correlated with each other.

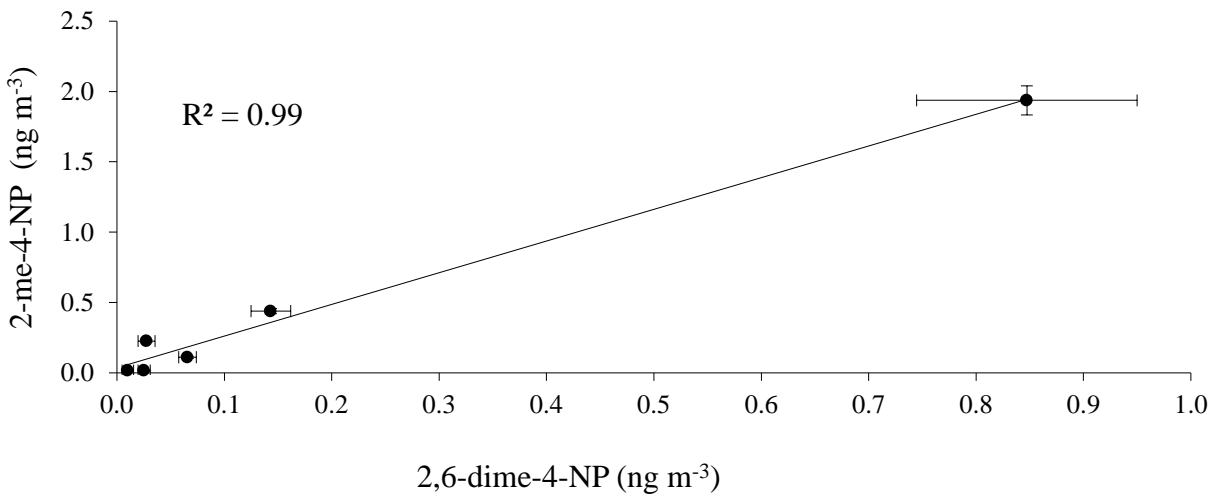
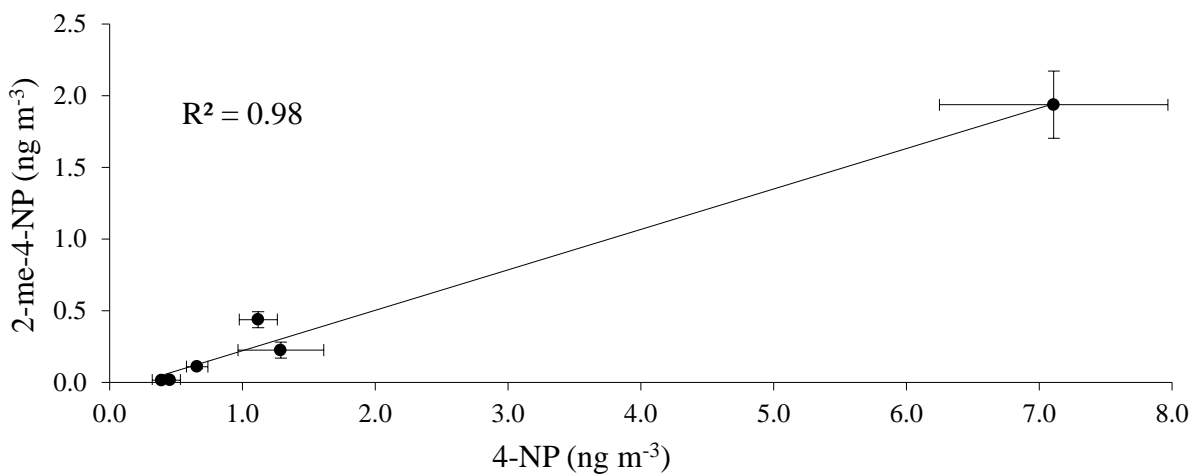
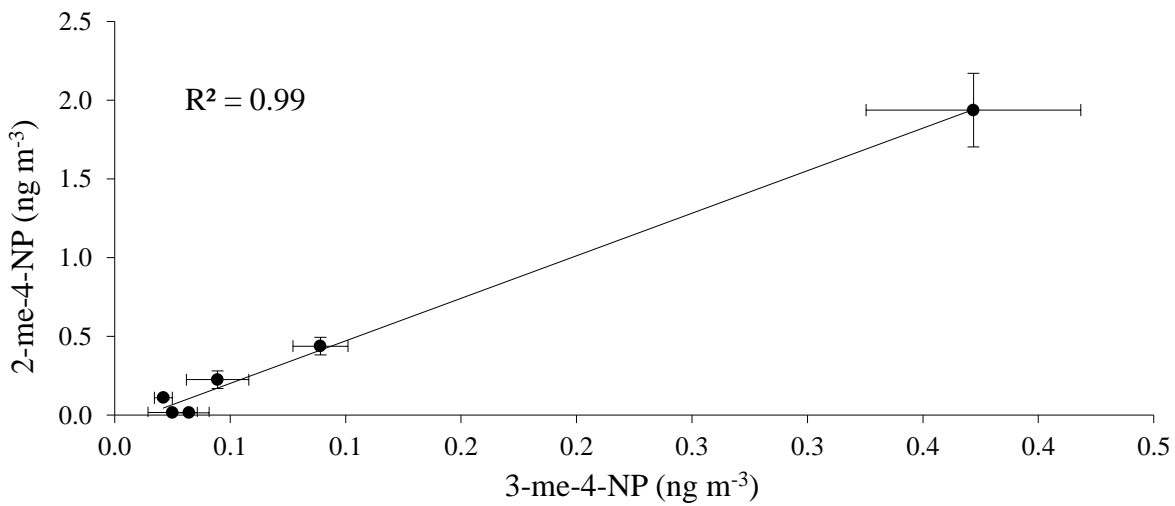


Figure 5.13: Correlation between the concentration of 2-me-4-NP and other target nitrophenols. The error bars are the uncertainty of the measurements.

Several lower molecular mass PAHs also showed a good correlation with SO₂ and CO, weak correlation with NO₂ and CH₄, but no correlation with CO₂. Hsu et al. (2015) also reported a strong correlation between PAHs and both SO₂ and NO₂. Based on their findings Hsu et al. (2015) suggested that emissions from industrial stacks as well as heavy hauler mine fleets might be the main sources of PAHs in this region. Moreover, strong correlation was noticed between PAHs and both toluene and p,m-xylene. In addition to possible co-emission of these compounds from upgrading facilities, they may also be co-emitted from tailing-ponds. This is due to the fact that both the aromatic VOCs and PAHs are suggested to be present in significant amounts within the tailing-ponds as a result of incomplete bitumen and solvent recovery during the Oil Sands processing (Siddique et al., 2006, Small et al., 2015). Therefore, the strong correlation observed suggests that these compounds are emitted from Oil Sands related activities. However, based on the limited number of data and information available it is difficult to distinguish between different sources due to co-located emissions.

In the case of n-alkanes, moderate correlation was noticed between several low molecular mass compounds (C₁₄ to C₁₈) and SO₂ and NO₂ but no significant correlation was observed with CO, CO₂, CH₄ and aromatic VOCs. The correlation observed suggests that these n-alkanes are to some extent emitted from Oil Sands related activities. However, the existence of significant positive axis intercepts for the correlation of many n-alkanes with NO₂ and SO₂, an example of which is shown in Figure 5.14, strongly suggests that there is also substantial impact from other sources, which is consistent with the CPI values.

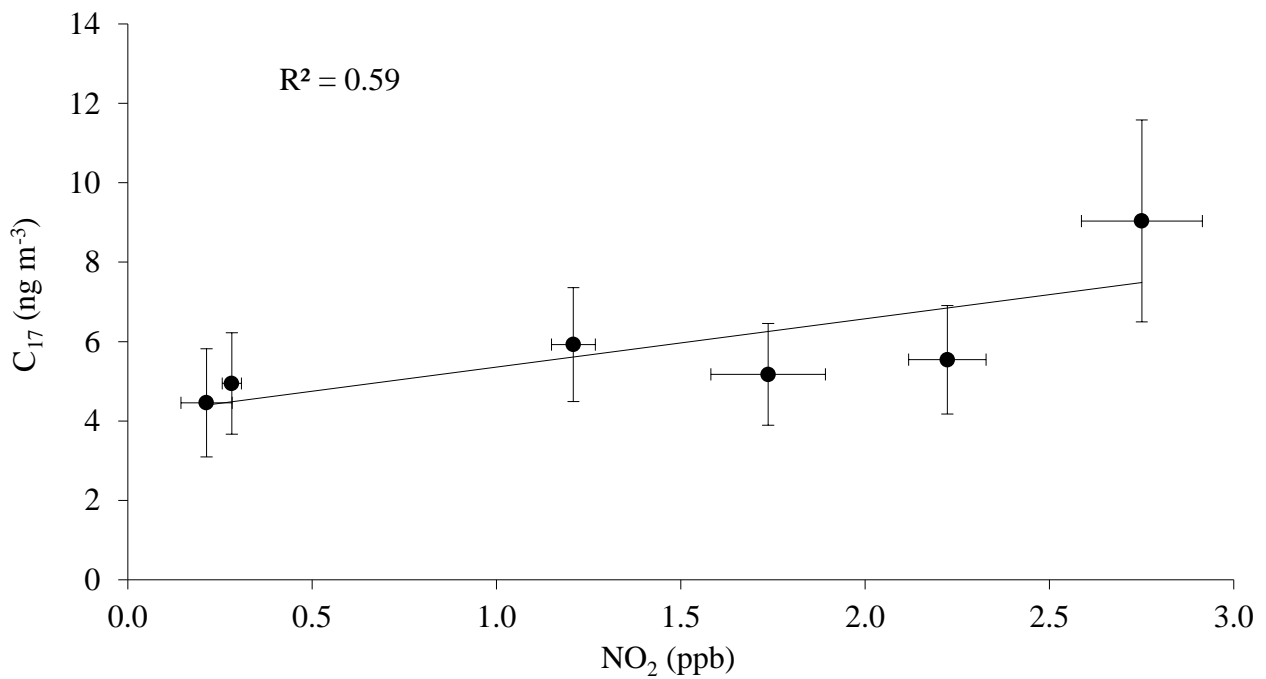
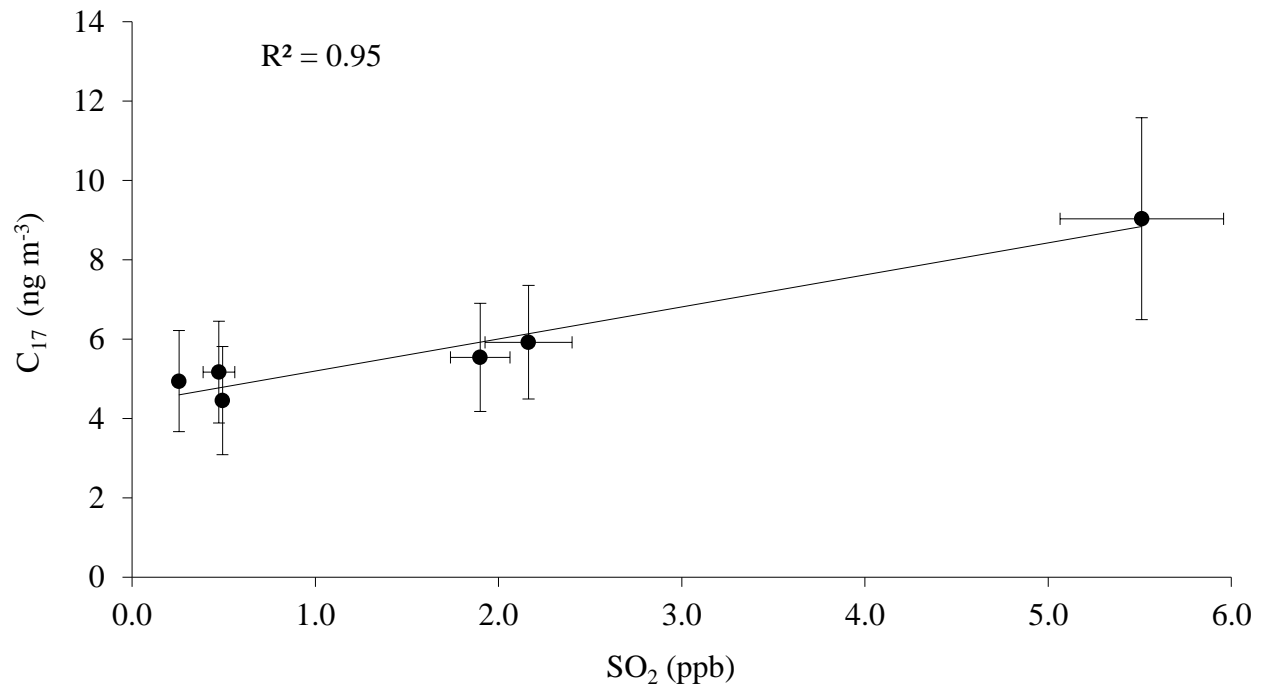


Figure 5.14: Correlation between the ambient concentrations of C_{17} and SO_2 (top) and NO_2 (bottom) mixing ratios. The error bar on the y-axis is the uncertainty of the measurements and the error bar on the x-axis is the error of the mean.

5.4 Atmospheric SVOC Concentration Measurements for Toronto

The ambient concentration of total (gas phase and PM) for target nitrophenols, n-alkanes and PAHs obtained from Toronto samples are summarized in Tables 4.19, 4.20 and 4.21, respectively. The nitrophenol concentration levels found in this work were generally within the same range as the levels found by previous studies in Dr. Rudolph's group using high volume filter sampling at York University (Table 5.3).

Table 5.3: Ambient concentrations of target nitrophenols found in this study compared to concentration levels found by other studies in Dr. Rudolph's group using the same sampling technique.

Compound	High Volume SIF (ng m ⁻³) ^a		High Volume SIF (ng m ⁻³) ^b		High Volume SIF (ng m ⁻³) ^c	
	Average	Range	Average	Range	Average	Range
4-me-2-NP	5.99	0.02 – 14.52	2.78	0.01 – 21.52	0.80	0.003 – 2.83
4-NP	13.46	2.3 – 19.63	6.88	0.61 – 18.57	3.43	0.78 – 7.64
3-me-4-NP	2.35	0.09 – 4.57	1.09	0.11 – 4.32	0.39	0.11 – 1.47
2-me-4-NP	3.92	0.35 – 9.04	3.22	0.19 – 8.51	0.91	0.21 – 2.88
2,6-dime-4-NP	0.98	0.10 – 2.79	1.06	0.05 – 5.44	0.44	0.06 – 1.26

^a Results based on five samples from this study

^b Results based on 27 samples acquired by Saccon (2013)

^c Results based on 16 samples acquired by Facca (2013)

The average concentration levels found in this work, however, were relatively higher, which might be a consequence of different sampling times. For example, most of the Toronto samples in this study were collected during the winter months. As such, the relatively higher concentrations observed may be attributed to higher pollution levels due to lower atmospheric mixing during winter months. The average concentrations of both

NO₂ and PM_{2.5} were also found to be higher for the samples collected during winter (see Appendix C). This result is consistent with the findings reported by Saccon et al. (2013) who observed correlation between target nitrophenols and NO₂ as well as PM_{2.5} concentrations. The average nitrophenol values found in this study are similar to the levels found by Nishioka and Lewtas (1992) but significantly different than the results reported by Cecinato et al. (2005) who found nitrophenols to be present predominantly in PM.

For PAHs, higher ambient concentrations were found for the lower molecular mass compounds including NAP, ACE, FLU and PHE. The ambient concentration levels found in this study were similar to those reported by Cothman and Bidleman (1995) and Mandalakis et al. (2002) who measured the ambient PAHs at a rural and a sub-urban site, respectively. The concentration levels found in the present study, however, were significantly lower than those reported for various urban sites in the literature (see Table 2.5). It is worth mentioning that a direct comparison of ambient PAH concentrations with different urban environments is difficult since the ambient concentrations of these compounds can significantly be impacted by the proximity of the sampling site to the emission sources. Moreover, due to increasing efforts to reduce anthropogenic emissions of PAHs in the last decades, contemporary ambient concentration of these compounds may have declined substantially compared to those from 15 to 20 years ago (Menichini, 1992; Dann, 1998). As such, it may not be surprising that the ambient concentrations of PAHs obtained in this study are lower than those reported in the studies that were performed many years back.

The ambient concentrations obtained for most n-alkanes in this work were similar to those reported by Mandalakis et al. (2002) except for the lower molecular mass n-alkanes, which were found to be significantly higher in this work. It should be noted that the concentration values for the lighter n-alkanes in this study have higher uncertainty and might not be accurately quantified due to not using the correct internal standard for their measurements. The CPI values for the n-alkanes for the Toronto sample in this study were between 0.91 and 1, which is in agreement with petroleum related emissions.

5.4.1 Atmospheric Phase Distribution Measurements of SVOCs

Sampling gas phase and PM together and PM alone using the high volume parallel sampling technique can be used to estimate the relative concentration of SVOCs in PM and gas phase assuming that the uncoated QFF collects PM only and XAD-4TM SIF collects both gas phase + PM. The high volume sampling technique and a denuder sampling method were used by previous studies in Dr. Rudolph's group in order to measure the phase distribution of nitrophenols in the atmosphere. The results from these studies showed that all target nitrophenols are predominantly found in the gas phase regardless of the measurement technique used. This finding was unexpected since the target nitrophenols selected cover a wide range of vapour pressures and if dependence on vapour pressure exists, it should clearly be noticeable. In order to determine whether this behavior is specific to this class of SVOCs, the phase partitioning of nitrophenols were compared to PAHs and n-alkanes. The phase partitioning measurements for the selected classes of SVOCs were obtained from the same sampling event and in doing so the

impacts from meteorological factors as well as the $PM_{2.5}$ concentrations or PM composition that can vary from sample to sample were eliminated. The results for PM and PM + gas phase concentrations for each class of SVOC obtained from three parallel samplings are summarized in Tables 4.22, 4.23 and 4.24. The phase distribution for the target PAHs, n-alkanes and nitrophenols are shown in Figures 5.15, 5.16 and 5.17, respectively.

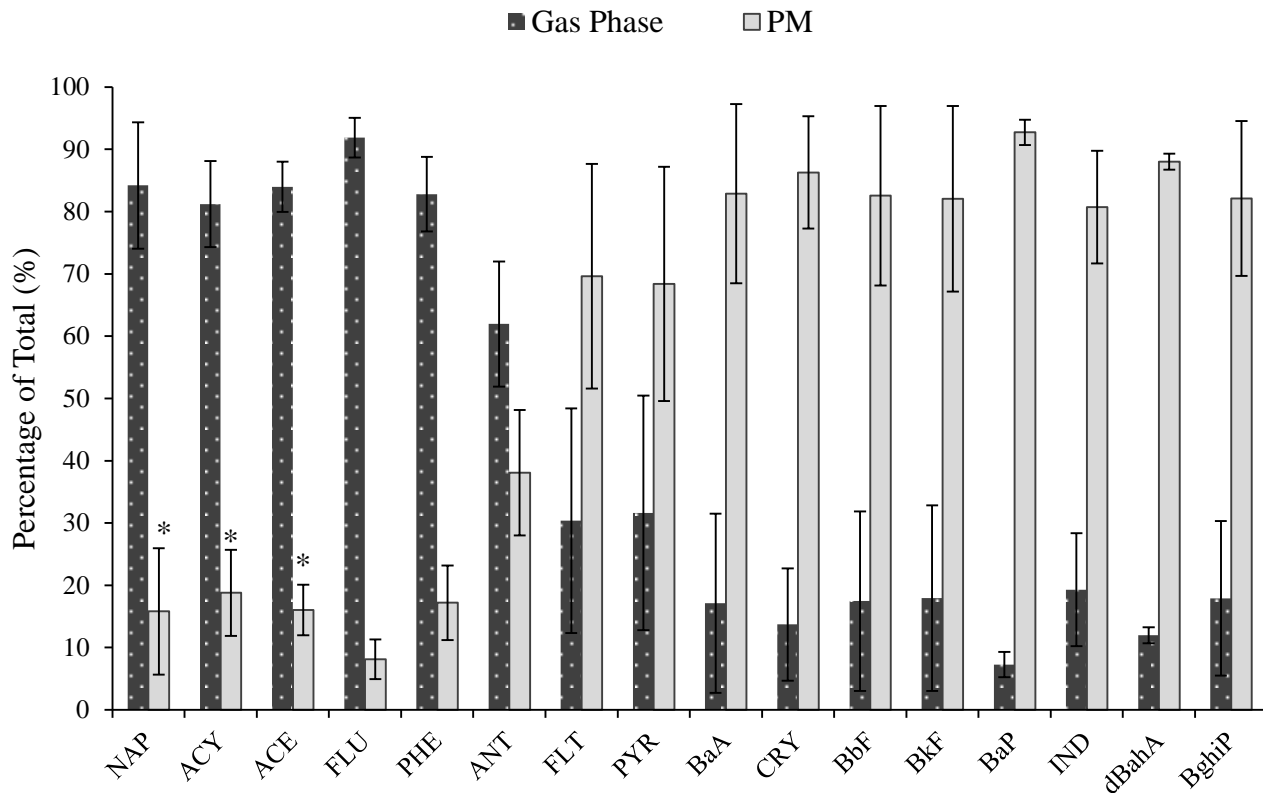


Figure 5.15: Average gas phase and PM distribution of individual PAHs obtained from three parallel sampling measurements. Percentage in PM and gas phase were obtained according to Eq. 4.5 and 4.6, respectively. The error bars represent the error of the mean. The concentrations marked with (*) are the upper limits.

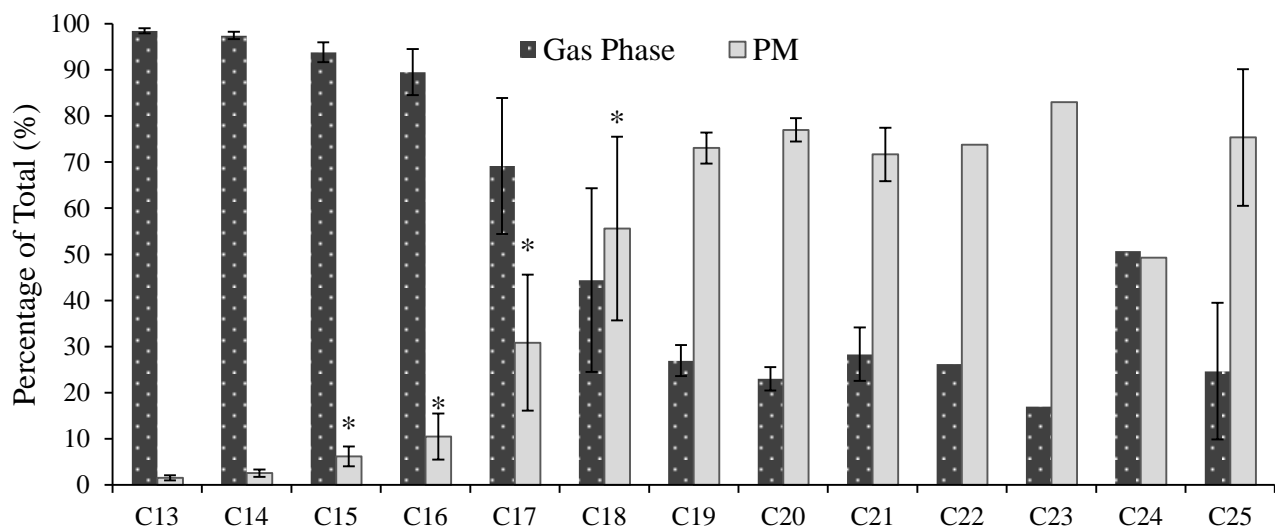


Figure 5.16: Average gas phase and PM distribution of individual n-alkanes obtained from three parallel sampling measurements. Percentage in PM and gas phase were obtained according to Eq. 4.5 and 4.6, respectively. The error bars represent the error of the mean. The concentrations marked with (*) are the upper limits.

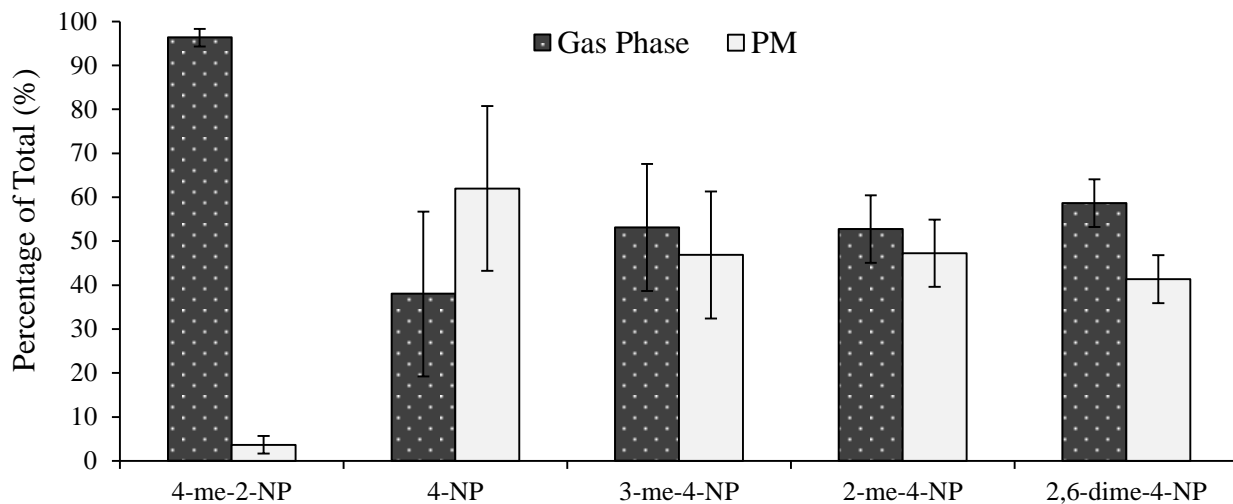


Figure 5.17: Average gas phase and PM distribution of individual nitrophenols obtained from three parallel sampling measurements. Percentage in PM and gas phase were obtained according to Eq. 4.5 and 4.6, respectively. The error bars represent the error of the mean.

From the results it can be seen that for both PAHs and n-alkanes lower molecular mass compounds are mainly found in the gas phase, whereas the higher molecular mass and less volatile compounds exhibit a greater association with the particulate phase. This finding is consistent with the results from other studies (Odabasi et al., 1999; Bi et al., 2003; Mandalakis et al., 2003; Possanzini et al. 2004; Cincinelli et al., 2007). In the case of nitrophenols, contrary to what was expected, most target nitrophenols – with the exception of 4-me-2-NP, which has the highest vapour pressure – did not show the expected increase in the particle phase as a result of decrease in the vapour pressure. This is analogous to the results obtained by previous studies in Dr. Rudolph's group (Facca, 2013; Saccon et al., 2013). The comparison between phase partitioning and vapour pressure dependence for the three classes of SVOCs is shown more clearly in Figure 5.18. From the results it can be seen that unlike nitrophenols, all n-alkanes and most PAHs show systematic dependence between phase partitioning and vapour pressure. Also, most target nitrophenols appeared to be found less in PM than the non-polar compounds with similar vapour pressure. However, from the target PAHs studied, a significant difference in phase partitioning was noticed for ANT and FLT even though their vapour pressures are not significantly different. This indicates that unlike for PAHs with relatively higher and lower volatilities – that are mainly found in gas phase and PM, respectively – the compounds with intermediate vapour pressures do not always show the partitioning expected from their vapour pressure. This may be due to structural or polarity differences that exist among some PAHs.

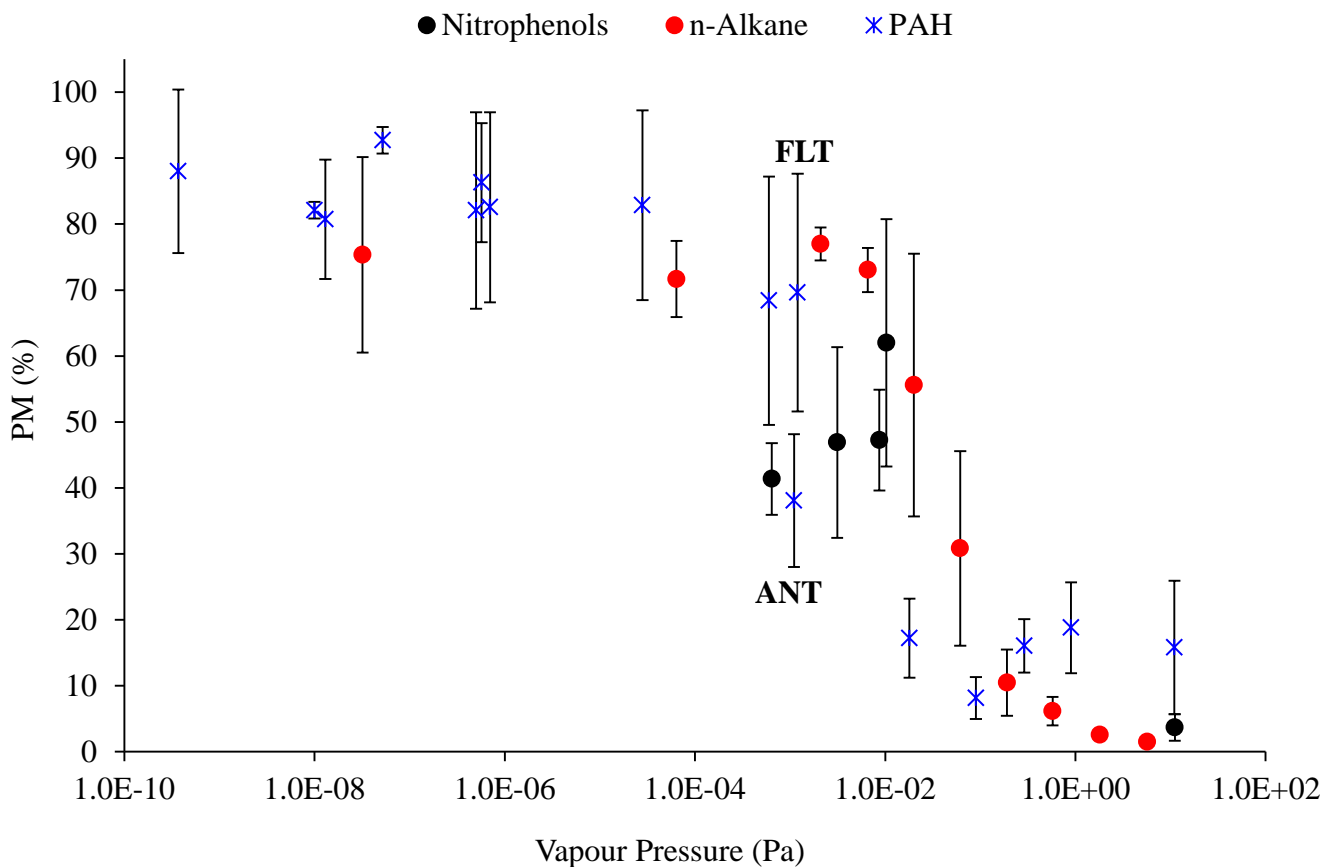


Figure 5.18: Average PM percentage for individual PAHs, n-alkanes, and nitrophenols obtained from three measurements plotted against vapour pressure. The error bars represent error of the mean. The PM percentage for some PAHs (NAP, ACE, ACY) and n-alkanes (C_{15} to C_{17}) are the upper limits.

Figure 5.19 presents the percentage in PM for individual PAHs, n-alkanes and nitrophenols plotted against their respective molecular mass. This plot shows that most nitrophenols partition more into PM compared to the PAHs with similar molecular mass. This is contrary to the plot with vapour pressure, which indicated that nitrophenols are found in PM less than the non-polar compounds. In addition, some PAHs also appeared to partition stronger into PM than the n-alkanes with similar molecular mass. These

results therefore suggest that the phase partitioning of most target nitrophenols and some PAHs are most likely influenced by their polarity or structure and that vapour pressure or molecular mass only provide rough approximations of phase partitioning.

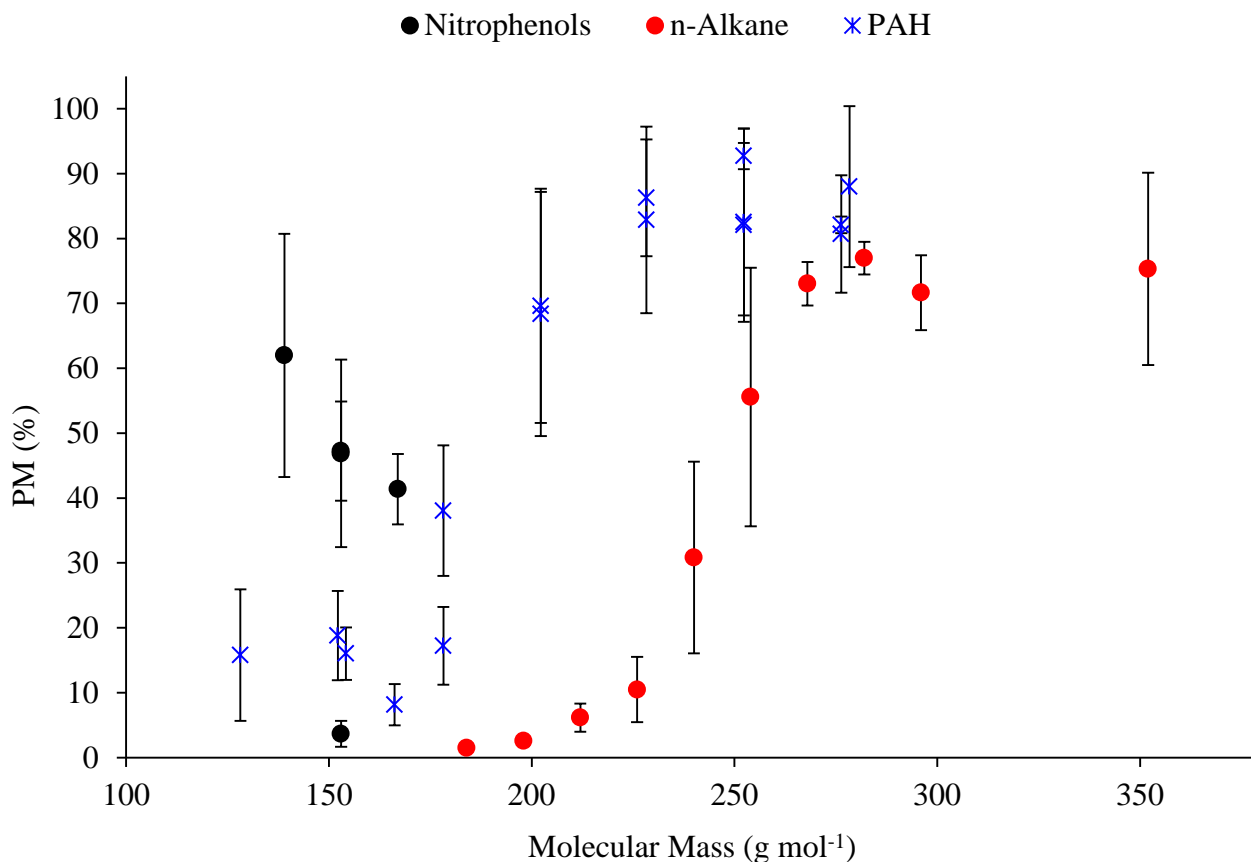


Figure 5.19: Average PM percentage for individual PAHs, n-alkanes, and nitrophenols obtained from three measurements plotted against their respective molecular mass. The error bars represent error of the mean. The PM percentage for some PAHs (NAP, ACE, ACY) and n-alkanes (C₁₅ to C₁₇) are the upper limits.

6 Conclusions and Future Work

The XAD-4TM SIF technique, originally developed and tested for nitrophenols, was modified and validated for sampling and analyzing other classes of SVOCs like PAHs and n-alkanes. The method validation tests were performed to assess the blank value, extraction and sampling efficiency of PAHs and n-alkanes on the XAD-4TM SIF. The atmospheric blank values of n-alkanes on XAD-4TM SIF were found to be in the sub-to-low ng m⁻³ range, which are significantly lower than the ambient concentration of these compounds observed on both Toronto and Oil Sands samples. In the case of PAHs, the atmospheric blank values were in the pg m⁻³ range for the target PAHs except for NAP, ACE, FLU and PHE. Overall, the ambient concentrations of all target PAHs determined in this work, apart from NAP, were found to be well above the blank values.

The collection efficiency of XAD-4TM SIF for PAHs and n-alkanes was found to be greater than 80 %. The average recoveries from spiked filters were between 43 % and 69 % for PAHs and between 45 % and 77 % for most n-alkanes. Relatively lower recoveries were observed for lighter and heavier n-alkanes. The lower recovery of the higher volatility n-alkanes is more likely a consequence of the volume reduction step during the filter extraction procedure. In the case of heavier n-alkanes, the lower recovery is most likely due to the stronger retention of these compounds by the XAD-4TM adsorbent. One suggestion for future studies would be to increase the number of extraction steps as well as the sonication time or use other extraction techniques (e.g. Soxhlet extraction or accelerated solvent extraction) to determine whether or not the recoveries improve for these compounds. Another recommendation would be to use a

range of deuterated internal standards that are specific to each of the target n-alkanes instead of only one that is currently used.

Ambient samples from both Toronto and the Alberta Oil Sands region were analyzed using the modified method. From the analysis of the Oil Sands samples it was found that the ambient concentrations of PAHs, n-alkane and nitrophenols were generally higher for the samples influenced by the plume episodes from nearby upgrading and refining facilities. Also, the CPI values obtained for the Oil Sands samples were in the range of 0.93 to 1.80, which indicated that the n-alkane emissions at the Oil Sands region are subjected to substantial emissions from petroleum related sources or biomass burning. However, some samples were also influenced by biogenic emissions. Furthermore, the ambient concentration of PHE was found to be significantly higher at the AMS-13 relative to the other AMSs in the Oil Sands region reported by Hsu et al. (2015) and compared to the levels found in Toronto. Comparison of the ambient concentration for target nitrophenols from Oil Sands to Toronto samples showed similar concentration abundances indicating that nitrophenols found in the Oil Sands region may be produced from the same precursor as in Toronto.

All nitrophenols and several low molecular mass PAHs and n-alkanes showed strong correlation with SO₂ suggesting presence of co-located sources. Also, since SO₂ is mainly emitted from industrial stacks in the Oil Sands region, these SVOCs could be from the same upgrading/refining facilities. Moreover, as was expected, correlations were noticed between nitrophenols and NO₂ as well as with aromatic VOCs (toluene, p,m-xylene, and benzene). This implies the Oil Sands mining and upgrading activities result in significant atmospheric nitrophenol concentrations, which are in some cases close to

levels found in urban areas such as Toronto. However, with the small data set and information available, it is difficult to draw clear conclusions whether nitrophenols were emitted from primary sources or formed via photo-oxidation of VOCs in the atmosphere. Furthermore, the dependence between a precursor and product cannot be easily distinguished from co-located emissions. PAHs also showed a strong correlation with both toluene and p,m-xylene. Therefore it can be concluded that these SVOCs are indeed emitted from Oil Sands related activities. However, due to the limited number of samples it is difficult to determine their specific source. Thus, to investigate possible emission sources of these SVOCs, ambient samples should be taken very close to the potential sources. In addition, measurements near emission sources may provide information on whether nitrophenols are emitted from primary sources or formed through secondary processes in the atmosphere. Alternatively, ambient measurements performed with high time resolution coupled with wind direction measurements further away from emission sources may also provide more insight regarding the specific sources of these SVOCs.

The phase distribution measurements of the three classes of SVOCs performed in this work provided additional insight into the partitioning of nitrophenols compared to other classes of SVOCs. For example, like nitrophenols, the phase distribution for some PAHs in the semi-volatile range did not follow the pattern expected from their vapour pressure. This indicates that in the semi-volatile range the phase partitioning of some compounds are not strictly influenced by their vapour pressures. And factors such as compound structure or polarity may play a major role on phase partitioning of these compounds. Given that these measurements were mainly performed during winter, it is recommended that ambient samples be obtained throughout the year to examine possible

changes in phase distribution of the selected classes of SVOCs under different atmospheric conditions. This will, in turn, provide more information regarding the impact of the physical-chemical properties of these compounds on phase partitioning.

To summarize, the main goal of this project, which was to develop and validate the suitability of the XAD-4TM SIF technique for concentration measurement of PAHs and n-alkanes, has been accomplished. Moreover, the preliminary results with respect to the ambient concentration of the three classes of SVOCs in the Oil Sands region were obtained, as were new insights regarding the phase partitioning of nitrophenols compared to other classes of SVOCs.

References

- Alberta environment and water: Oil Sands information portal. **c1995-2015**.
<http://osip.alberta.ca/map/> (accessed June 16th 2015).
- Alberta energy Oil Sands: Facts and statistics. **c1995-2015**.
<http://www.energy.alberta.ca/oilsands/791.asp> (accessed June 16th 2015).
- Andino, J. M., Smith, J. N., Flagan, R. C., Goddard III, W. A. and Seinfeld, J. H.:
Mechanism of atmospheric photo-oxidation of aromatics: a theoretical study. *J. Phys. Chem.*: **1996**, 100: 10967-10980.
- Araki Y., Tang N., Ohno M., Kameda T., Toriba A., Hayakawa K.: Analysis of
atmospheric polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic
hydrocarbons in gas/particle phases separately collected by a high volume air
sampler equipped with a column packed with XAD-4TM Resin. *J. Health Sci.*,
2009, 55 1: 77-85.
- Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds, *J. Phys. Chem. Ref. Data*, **1994**, 2: 1-216.
- Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, *Atmos. Environ.*, **2000**, 34: 2063-2101.
- Bi, X., Sheng, G., Peng, P., Chen, Y., Zhang, Z., and Fu, J.: Distribution of particulate
and vapor-phase n-alkanes and polycyclic aromatic hydrocarbons in urban
atmosphere of Guangzhou, China. *Atmos. Environ.*, **2003**, 37: 289-298.
- Bi, X., Sheng, G., Peng, P., Chen, Y., and Fu, J.: Size distribution of n-alkanes and
polycyclic aromatic hydrocarbons (PAHs) in urban and rural atmospheres of
Guangzhou, China. *Atmos. Environ.* **2005**, 39 (3): 477-487.
- Bidleman, T. F.: Atmospheric processes: Wet and dry deposition of organic compounds
are controlled by their vapor-particle partitioning. *Environ. Sci. Technol.*, **1988**,
22(4): 361-367.
- Bolzacchini, E., Bruschi, M., Hjorth, J., Meinardi, S., Orlandi, M., Rindone, B. and
Rosenbohm, E.: Gas-phase reaction of phenol with NO₃. *Environ. Sci. Technol.*, **2001**, 35: 1791-1797.
- Busca, R. S.: Method development for the sampling and analysis of atmospheric
nitrophenols. MSc Thesis. York University, **2010**.

- Cecinato, A., Di Palo, V., Pomata, D., Scianò, M. C. T. and Possanzini, M.: Measurement of phase-distributed nitrophenols in Rome ambient air. *Chemos.*, **2005**, 59: 679-683.
- Cincinelli, A., Bubba, M. D., Martellini, T., Gambaro, A., and Lepri, L.: Gas-particle concentration and distribution of n-alkanes and polycyclic aromatic hydrocarbons in the atmosphere of Prato (Italy). *Chemos.*, **2007**, 68: 472-478.
- Chow, J.: Measurement methods to determine compliance with ambient air quality standards for suspended particles, *J. Air Waste. Manage.*, **1995**, 45, 320-382.
- Cotham, W. E. and Bidleman, T. F.: Polycyclic aromatic hydrocarbons and polychlorinated biphenyls at an urban and a rural site near Lake Michigan. *Environ. Sci. Tech.*, **1995**, 29: 2782-2789.
- Daignault, S. A., Noot, D. K., Williams, D. T., and Huck, P. M.: A review of the use of XAD resins to concentrate organic compounds in water. *Water Res.*, **1988**, 22(7): 803-813.
- Dann, E. Environment Canada, Ambient air measurements of polycyclic aromatic hydrocarbons (PAH), polychlorinated dibenzo-pdioxins (PCDD) and polychlorinated dibenzofurans in Canada (1987–1997). *Environ. Technol. Center Report*. [http:// www.etc-cte.ec.gc.ca/publications/recent/pah_report_e.html](http://www.etc-cte.ec.gc.ca/publications/recent/pah_report_e.html).
- Eichmann, R., Neuling, P., Ketseridis, G., Hahn, J., Jaenicke, R., and Junge, c.: n-Alkane studies in the troposphere-1. gas and particulate concentrations in north atlantic air. *Atmos. Environ.*, **1979**, 13(5): 587-599.
- Eiguren-Fernandez, A., Miguel, A. H., Froines, J. R., Thurairatnam, S., and Avol, E. L.: Seasonal and spatial variation of polycyclic aromatic hydrocarbons in vapor-phase and PM_{2.5} in southern California urban and rural communities. *Aerosol Sci. Technol.*, **2004**, 38(5): 447-455.
- Facca, C.: Method development of a denuder based technique for the determination of the partitioning of nitrophenols, M.S. thesis, York University, Toronto, ON, **2013**.
- Finlayson-Pitts, B. J. and Pitts, J. N., Jr.: *Chemistry of the upper and lower atmosphere: theory, experiments and applications*. San Diego: Academic Press, **2000**.
- Forstner, H., Flagan, R., Seinfeld, J.: Secondary organic aerosol from the photo-oxidation of aromatic hydrocarbons: molecular composition. *Environ. Sci. Technol.*, **1997**, 31(5): 1345-1358.

- Galarneau, E., Hollebone, B. P., Yang, Z., and Schuster, J.: Preliminary measurement-based estimates of PAH emissions from oil sands tailings ponds. *Atmos. Environ.* **2014**, 97: 332-335.
- Gensch, I., Kiendler-Scharr, A., and Rudolph, J. Isotope ratio studies of atmospheric organic compounds: principles, methods, applications and potential. *Int. J. Mass Spectrom.*, **2014**, 365-366, 206-221.
- Goldstein, A., Shaw, S. Isotopes of volatile organic compounds: an emerging approach for studying atmospheric budgets and chemistry. *Chem. Rev.*, **2003**, 103: 5025-5048.
- Gong, X.: private communication.
- Government of Canada and Government of Alberta, **2013**. Ec.gc.ca - /data_donnees/SSB OSM_Air/AmbientGasesAndParticles/Aircraft/Aircraft_2013/. Ec.gc.ca - /data_donnees/SSBOSM_Air/AmbientGasesAndParticles/Aircraft/Aircraft_2013/. (accessed August July 15th 2015).
- Gundel, L. and Hering, S. V. Absorbing filter media for denuder-filter sampling of total organic carbon in airborne particles. Record of Invention WIB 1457, Lawrence Berkeley National Laboratory (USA), **1998**.
- Gundel, L. and Lane, D.: Sorbent-coated diffusion denuders for direct measurement of gas-particle partitioning by semi-volatile organic compounds, in: Lane, D.: Gas and particle phase measurements of atmospheric organic compounds, Gordon and Breach Science Publishers, Canada, **1999**, 287-332.
- Herterich, R. and Herrmann, R.: Comparing the distribution of nitrated phenols in the atmosphere of two German hill sites. *Environ. Technol.*, **1990**, 11: 961-972.
- Hsu, Y. -, Harner, T., Li, H., and Fellin, P.: PAH measurements in air in the Athabasca Oil Sands region. *Environ. Sci. Technol.* **2015**, 49(9): 5584-5592.
- Hunt G. and Pangaro N.: Potential contamination from the use of synthetic adsorbents in air sampling procedures. *Analyt. Chem.* **1982**, 54: 369-372.
- Inomata, S., Tanimoto, H., Fujitani, Y., Sekimoto, K., Sato, K., Fushimi, A., Yamada, H., Hori, S., Kumazawa, Y., Shimono, A., Hikida, T.: On-line measurements of gaseous nitro-organic compounds in diesel vehicle exhaust by proton-transfer-reaction mass spectrometry. *Atmos. Environ.*, **2013**, 73: 195-203.

- Inomata, S., Fushimi, A., Sato, K., Fujitani, Y., Yamada, H.: 4-nitrophenol, 1-nitropyrene, and 9-nitroanthracene emissions in exhaust particles from diesel vehicles with different exhaust gas treatments, *Atmos. Environ.*, **2015**, 110: 93-102.
- Irei, S.: Laboratory studies of stable carbon isotope ratio of secondary particulate organic matter in the gas phase. PhD Dissertation, York University, **2008**.
- James, H. A., Steel, C. P., and Wilson, I.: Impurities arising from the use of XAD-2 resin for the extraction of organic pollutants in drinking water. *J. Chromat.*, **1981**, 208(1): 89-95.
- Jang, M. and Kamens, R.M.: Characterization of secondary aerosol from the photo-oxidation of toluene in the presence of NO_x and 1-propene, *Environ. Sci. Technol.*, **2001**, 35: 3626-3639.
- Junge, C. E.: Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants. *Adv. Environ. Sci. Technol.*, **1977**, 8(1): 7-25.
- Junk G. A., Richard J. J., Griesei M. D., Witiak D., Witiak J. L., Arauello M. D., Vick R., Svec H. J., Fritz J. S. and Calder V.: Use of macro reticular-resins in the analysis of water for trace organic contaminants. *Chromat.*, **1974**, 99: 745-762.
- Kadowaki, S.: Characterization of carbonaceous aerosols in the Nagoya urban area. 2. behaviour and origin of particulate n-alkanes. *Environ. Sci. Technol.*, **1994**, 28: 129-135.
- Kelly, E. N., Short, J. W., Schindler, D. W., Hodson, P. V., Ma, M., Kwan, A. K., Fortin, B. L.: Oil Sands development contributes polycyclic aromatic compounds to the Athabasca River and its tributaries. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, 106 (52): 22346–22351.
- Keyte, I. J., Harrison, R. M., and Lammel, G.: Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons-a review. *Chem. Soc. Rev.*, **2013**, 42(24): 9333-9391.
- Kindzierski, W. B. and Ranganathan, H. K. S.: Indoor and outdoor SO₂ in a community near Oil Sands extraction and production facilities in northern Alberta, *J. Environ. Eng. Sci.*, **2006**, 5: S121–S129.
- Kiss, G., Varga-Puchony, Z., Rohrbacher, G., and Hlavay, J. Distribution of polycyclic aromatic hydrocarbons on atmospheric aerosol particles of different sizes. *Atmos. Res.*, **1998**, 46(3-4), 253-261.

- Knapp, D. R.: Handbook of analytical derivatization reaction. New York: Wiley and Sons, **1979**.
- Kurek, J., Kirk, J. L., Muir, D. C., Wang, X., Evans, M. S., Smol, J. P.: Legacy of a half century of Athabasca Oil Sands development recorded by lake ecosystems. Proc. Natl. Acad. Sci. U.S.A., **2013**, 110 (5): 1761–1766.
- Ladji, R., Yassaa, N., Balducci, C., and Cecinato, A.: Particle size distribution of n-alkanes and polycyclic aromatic hydrocarbons (PAHS) in urban and industrial aerosol of Algiers, Algeria. Environ. Sci. Pollut. Res., **2014**, 21(3): 1819-1832.
- Leal-Granadillo, I. A., Alonso, J. I. G., and Sanz-Medel, A.: Determination of n-alkanes and polycyclic aromatic hydrocarbons in atmospheric particulate and vapour phases in Oviedo, Spain, by GC-MS. J. Environ. Monit., **2000**, 2: 218-222.
- Li, X., Wang, Y., Guo, X., and Wang, Y.: Seasonal variation and source apportionment of organic and inorganic compounds in PM_{2.5} and PM₁₀ particulates in Beijing, China. J. Environ. Sci., **2013**, 25(4): 741-750.
- Mackay D, Shiu W Y, Ma K C.: Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. Volume II. Lewis Publishers, Michigan **1992**.
- Masclat, P., Mouvier, G., Nikolaou, K.: Relative decay index and sources of polycyclic aromatic hydrocarbons. Atmos. Environ., **1986**, 20: 439–446.
- Mandalakis, M., Tsapakis, M., Tsoga, A., and Stephanou, E. G.: Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs, and PCDD/Fs in the atmosphere of Athens (Greece). Atmos. Environ., **2002**, 36: 4023-4035.
- Mazurek, M., Cass, G., Simoneit, B.R.T.: Interpretation of high-resolution gas chromatography and high-resolution gas chromatography – mass spectrometry data acquired from atmospheric organic aerosol samples. Aerosol Sci. Technol., **1989**, 10: 408-420.
- McLaren, R.: private communication.
- Menichini, E. Urban air pollution by polycyclic aromatic hydrocarbons: Levels and sources of variability. Sci. Total Environ., **1992**, 116(1-2), 109-135.
- Morville, S., Scheyer, A., Mirabel, P. and Millet, M.: A multi-residue method for the analysis of phenols and nitrophenols in the atmosphere. J. Environ. Monitor., **2004**, 6: 963-966.

- Moukhtar, S., Saccon, M., Kornilova, A., Irei, S., Huang, L. and Rudolph, J.: Method for determination of stable carbon isotope ratio of methyl nitrophenols in atmospheric particulate matter. *Atmos. Meas. Tech.*: **2011**, 4: 2453-2464.
- Mugica, V., Hernández, S., Torres, M., and García, R.: Seasonal variation of polycyclic aromatic hydrocarbon exposure levels in Mexico City. *J. Air Waste Manage. Assoc.*, **2010** 60(5): 548-555.
- Nishioka, M. G. and Lewtas, J.: Quantification of nitro- and hydroxylated nitro-aromatic/polycyclic aromatic hydrocarbons in selected ambient air daytime winter samples. *Atmos. Environ.*, **1992**, 26A(11): 2077-2087.
- Nojima, K., Kawaguchi, A., Ohya, T., Kanno, S., Hirobe, M.: Studies on photochemical reaction of air pollutants. X.1) Identification of nitrophenols in suspended particulates, *Chem. Pharm. Bull.*, **1983**, 31: 1047-1051.
- Odabasi, M., Vardar, N., Sofuoglu, A., Tasdemir, Y., Holsen, T. M.: Polycyclic aromatic hydrocarbons (PAHs) in Chicago air. *Sci. Total Environ.*, **1999**, 227: 57-67.
- Pankow, J. F. Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmos. Environ.*: **1987**, 21(11): 2275-2283.
- Pankow, J. F. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmos. Environ.*: **1994**, 28(2): 185-188.
- Parajulee, A., and Wania, F.: Evaluating officially reported polycyclic aromatic hydrocarbon emissions in the Athabasca Oil Sands region with a multimedia fate model. *Proc. Natl. Acad. Sci. U.S.A.*, 2014, 111(9): 3344-3349.
- Park, S. S.; Kim, Y. J.; Kang, C. H.: Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. *Atmos. Environ.*, **2002**, 36: 2917-2924.
- Possanzini, M., Palo, V. D., Gigliucci, P., Sciano, M. C. T., Cecinato, A.: Determination of phase distributed PAH in Rome ambient air by denuder/GC-MS method. *Atmos. Environ.*, **2004**, 38: 1727-173.
- Rogge, W.F., Hildemann, L., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T.: Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy duty diesel trucks. *Environ. Sci. Technol.*, **1993a**, 27: 636-651.
- Rogge, W.F., Hildemann, L., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T.: Sources of fine organic aerosol: 4. particulate abrasion products from leaf surfaces of urban plants. *Environ. Sci. Technol.*, **1993c**, 27: 2700-2711.

- Rudolph, J., Czuba, E., Norman, A., Huang, L., and Ernst, D.: Stable carbon isotope composition of non-methane hydrocarbons in emissions from transportation related sources and atmospheric observation in an urban atmosphere. *Atmos. Environ.*, **2002**, 36: 1173-1181.
- Ruzicka, K. and Majer, V.: Simultaneous treatment of vapour pressures and related thermal data between the triple and normal boiling temperatures for n-alkanes C₅ - C₂₀. *J. Phys. Chem. Ref. Data*, **1994**, 23: 1-39.
- Sacson, M., Busca, R., Facca, C., Huang, L., Irei, S., Kornilova, A., Lane, D., and Rudolph, J.: Method for the determination of concentrations and stable carbon isotope ratios of atmospheric phenols. *Atmos. Meas. Tech. Discuss.*, **2013**, 6: 4705-4733.
- Shiu, W. and Ma, K.: Temperature dependence of physical - chemical properties of selected chemicals of environmental interest. I. mononuclear and poly-nuclear aromatic hydrocarbons. *J. Phys. Chem. Ref. Data*, **2000**, 29 (1): 41-130.
- Siddique, T., Fedorak, P. M., and Foght, J. M.: Biodegradation of short-chain n-alkanes in Oil Sands tailings under methanogenic conditions, *Environ. Sci. Technol.*, **2006**, 40: 5459–5464.
- Sigma-Aldrich Co. Amberlite XAD polymeric resins. Product Information, Missouri, United States of America, **1998**.
- Simoneit, B.R.T., Chester, R., Eglinton, G.: Biogenic lipids in particulates from the lower atmosphere over the eastern Atlantic. *Nature*. **1977**, 267: 682–685.
- Simoneit, B. R. T.: Organic matter of the troposphere – 3: characterization and sources of petroleum and pyrogenic residues in aerosols over the western United States, *Atmos. Environ.*, **1984**, 18(1): 51-67.
- Simpson, I. J., Blake, N. J., Barletta, B., Diskin, G. S., Fuelberg, H. E., Gorham, K., Blake, D. R.: Characterization of trace gases measured over Alberta Oil Sands mining operations: 76 speciated C₂-C₁₀ volatile organic compounds (VOCs), CO₂, CH₄, CO, NO, NO₂, NO_y, O₃ and SO₂. *Atmos. Chem. Phys.*, **2010**, 10(23): 11931-11954.
- Strausz, O. and Lown, E.: *The Chemistry of Alberta Oil Sands, Bitumen and Heavy Oils*, Alberta Energy Research Institute, Calgary, Alberta, **2003**.
- Dr. Strawbridge, K.: private communication.
- Tisch Environmental, Inc. Operations manual TE-6070-BL PM₁₀ particulate matter 10 microns and less MFC brushless high volume air sampler.

- Tremp, J., Mattrel, P., Fingler, S., Giger, W.: Phenols and nitrophenols as tropospheric pollutants: emissions from automobile exhausts and phase transfer in the atmosphere, *Water Air Soil Poll*, **1993**, 68: 113-123.
- U.S. Environment Protection Agency, Locating and estimating air emissions from sources of polycyclic organic matter, EPA-454/R-98-014, **1998**.
- Waters Corporation. Oasis Sample Extraction Products. Product Information, Massachusetts, United States of America, **2008**.
- Watson, J. G.; Chow, J. C.; Wang, X.; Zielinska, B.; Kohl, S. D.; Gronstal, S.: Characterization of real-world emissions from non-road mining trucks in the Athabasca Oil Sands region during September, 2009; Desert Res. Instit.: Fort McMurray, AB, **2013**.
- Yamasaki, H., Kuwata, K., Miyamoto, H.: Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.*, **1982**, 16: 189–194.
- Yang, C., Wang, Z., Yang, Z., Hollebone, B., Brown, C., Landriault, M., Fieldhouse, B.: Chemical fingerprints of Alberta Oil Sands and related petroleum products, *Environ. Foren.*, **2011**, 12: 173–188.
- Yang H. H., Lee W. J., Chen S.J., Lai S.O.: PAH emission from various industrial stacks. *J. Hazard Mater*, **1998**, 60:159–174.
- Zhao, J., Zhang, R., Misawa, K. and Shibuya, K.: Experimental product study of the HO initiated oxidation of m-xylene. *Photochem. Photobiol.*, **2005**, 176: 199-207.

Appendix

Appendix A: Sampling dates, times and sampling volumes.

Filter	Sampling Start		Sampling End		Sample Volumes (m ³)
	Date (dd/mm/yy)	Time	Date (dd/mm/yy)	Time	
T-X230713A-Top	23/07/13	1:00 pm	24/07/13	1:19 pm	1648.7
T-X230713A-Bottom	23/07/13	1:00 pm	24/07/13	1:19 pm	1648.7
OS-X010913C	01/09/13	10:50 am	02/09/13	5:50 am	1288.2
OS-X020913C	02/09/13	10:30 am	03/09/13	12:23 pm	1754.9
OS-X040913C	04/09/13	10:35 am	04/09/13	5:35 pm	474.6
OS-X060913C	06/09/13	1:30 pm	07/09/13	12:40 pm	1570.7
OS-X070913C	07/09/13	12:45 pm	08/09/13	12:06 pm	1603.5
OS-X080913C	08/09/13	12:34 pm	09/09/13	1:00 pm	1656.6
OS-X090913C	09/09/13	1:05 pm	09/09/13	11:05 pm	678
T-X291013A-Top	29/10/13	2:10 pm	30/10/13	11:25 am	1440.6
T-Q291013B-Bottom	29/10/13	2:10 pm	30/10/13	11:25 am	1440.7
T-Q051113A	05/11/13	3:25 pm	06/11/13	12:18 pm	1414.76
T-Q051113B	05/11/13	3:25 pm	06/11/13	12:18 pm	1414.76
T-Q051113C	05/11/13	3:25 pm	06/11/13	12:18 pm	1414.76
T-X121213A	12/12/13	11:36 am	13/12/13	10:27 am	1549.2
T-Q121213B	12/12/13	11:36 am	13/12/13	10:27 am	1549.2
T-X130114C	13/01/14	11:42 am	14/01/13	6:42 am	1288.2
T-SQ130114C	13/01/14	11:42 am	14/01/13	6:42 am	1288.2
T-X160215A	16/02/15	11:16 am	17/02/15	9:27 am	1504.0
T-Q160215B	16/02/15	11:16 am	17/02/15	9:27 am	1504.0
T-X230215A	23/02/15	12:09 pm	24/02/15	11:50 am	1614.8
T-Q230215B	23/02/15	12:09 pm	24/02/15	11:50 am	1614.8

Filter samples are labeled as follows:

Location-filter type-sampling date-air sampler used

T = Toronto

OS = Oil Sands

X = Stands for XAD-4TM SIF

Q = Stands for uncoated quartz fiber filter

SQ = Stands for slotted quart fiber filter

Sampling date: day/Month/Year

Appendix B: Pollution and wind direction data for Oil Sands Samples.

Filter	Average SO ₂ (ppb) ^(a)	Average NO ₂ (ppb) ^(a)	Average CO (ppb) ^(a)	Average CO ₂ (ppm) ^(a)	Average CH ₄ (ppb) ^(a)	Wind Direction (degree) ^(b)
X010913C	0.26	0.28	112.4	426.3	1980.3	224
X020913C	2.16	1.21	102.6	409.5	1967.1	173
X040913C	5.51	2.75	144.7	405.9	2172.2	208
X060913C	1.90	2.22	119.6	444.8	2090.6	183
X070913C	0.95	4.20	124.6	412.1	2096.0	190
X080913C	0.47	1.74	138.1	433.5	2228.7	210
X090913C	0.49	0.21	107.1	393.5	1887.8	175

Pollution and wind direction data are averaged over the sampling time.

^(a) Pollution data acquired by Dr. McLaren (private communication)

^(b) Wind direction data acquired by Dr. Strawbridge (private communication).

Filter samples are labeled as follows:

Location-filter type-sampling date-air sampler used

T = Toronto

OS = Oil Sands

X = Stands for XAD-4TM SIF

Q = Stands for uncoated quartz fiber filter

SQ = Stands for slotted quartz fiber filter

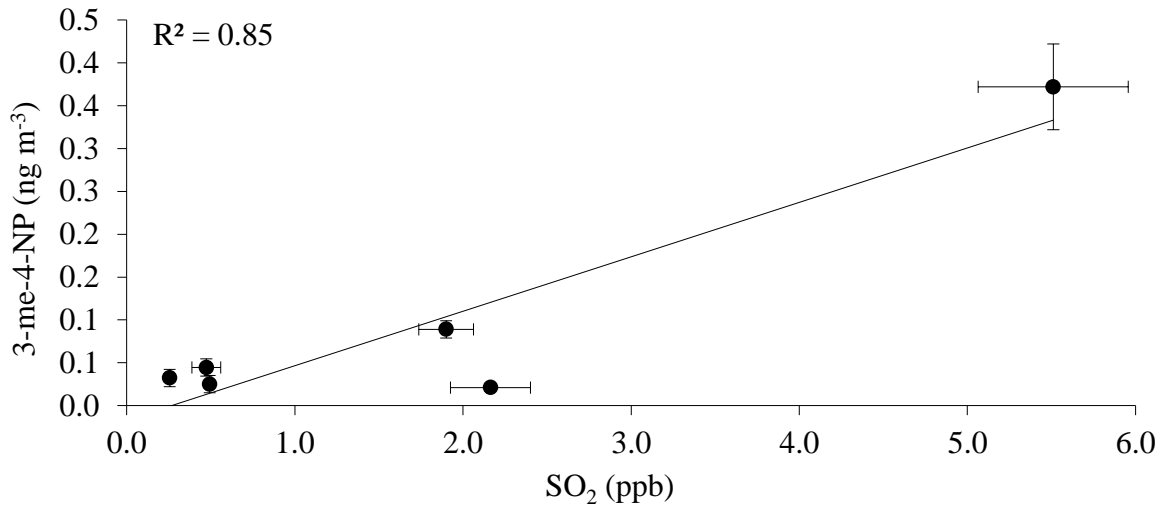
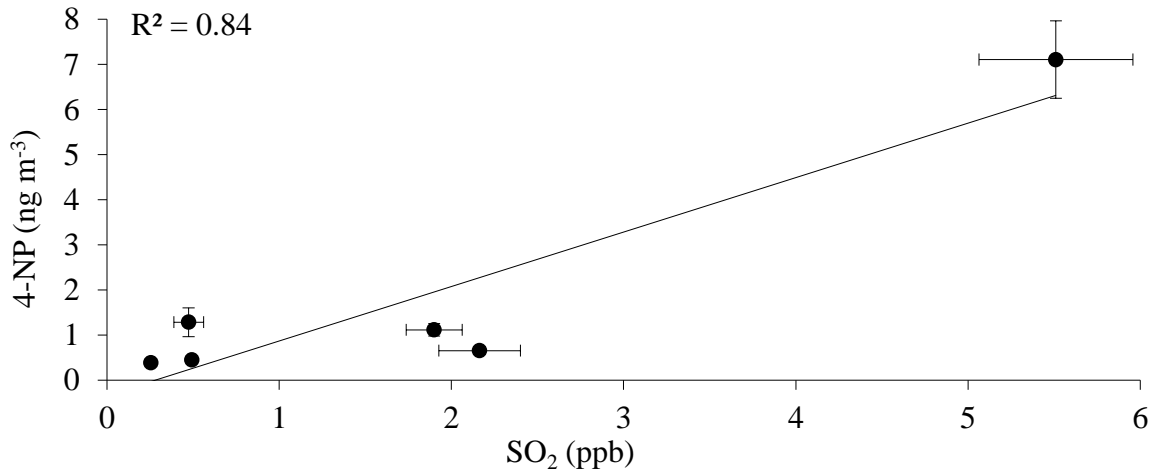
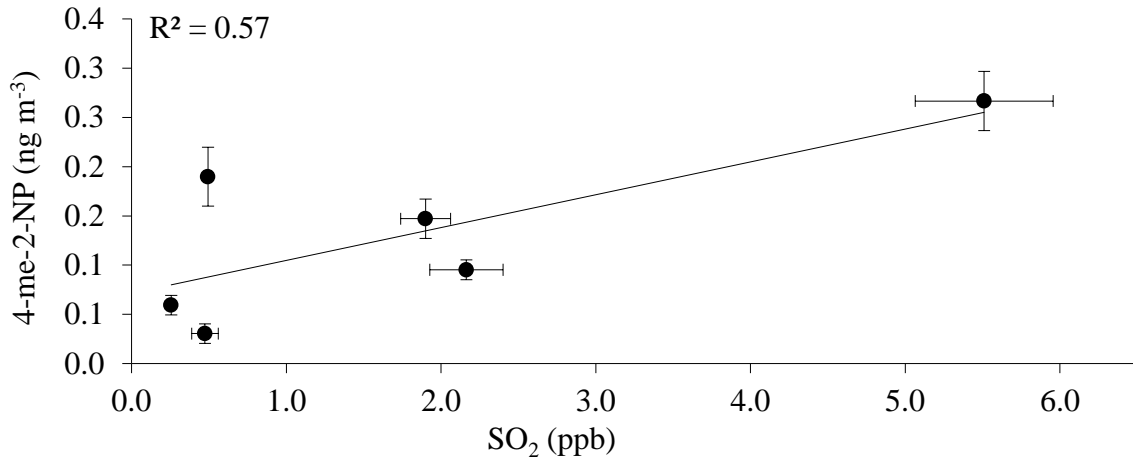
Sampling date: day/Month/Year

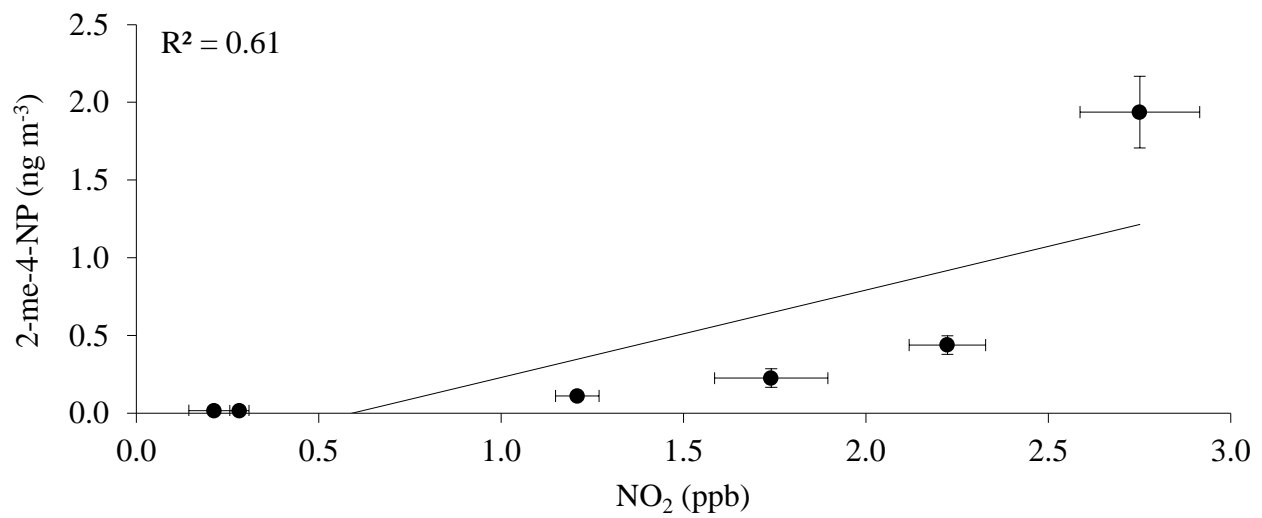
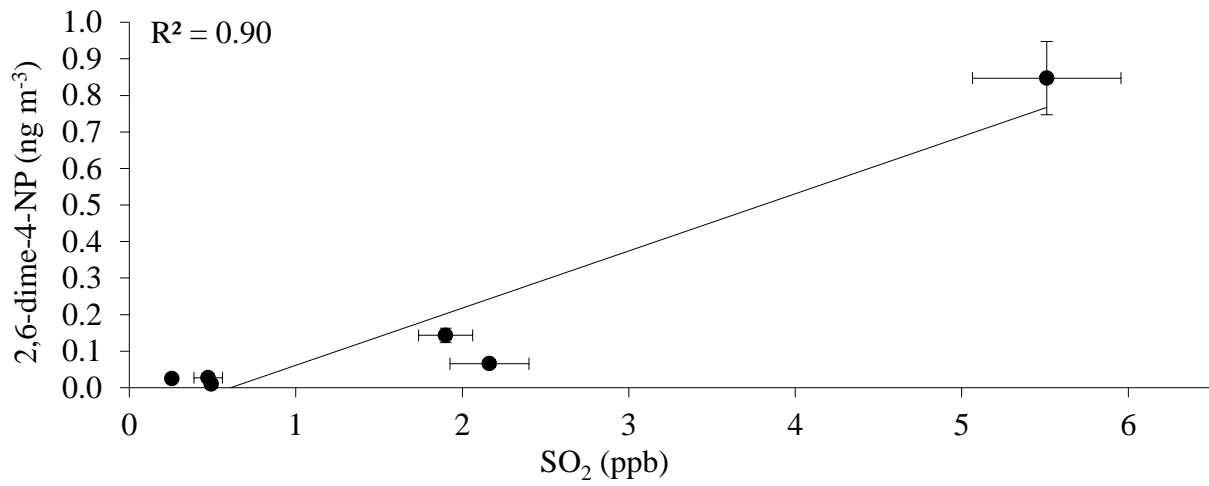
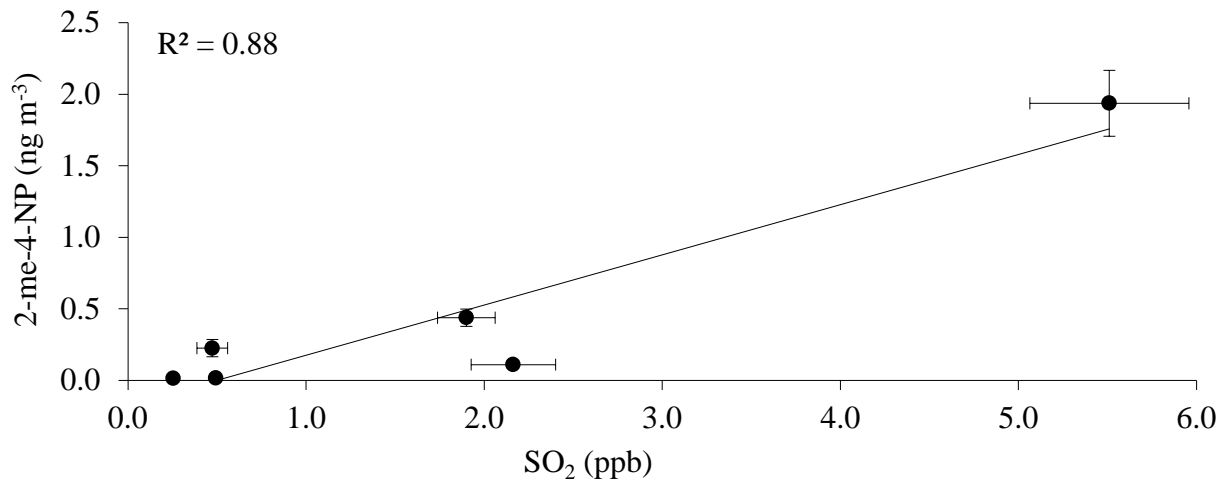
Appendix C: Pollution data for Toronto samples.

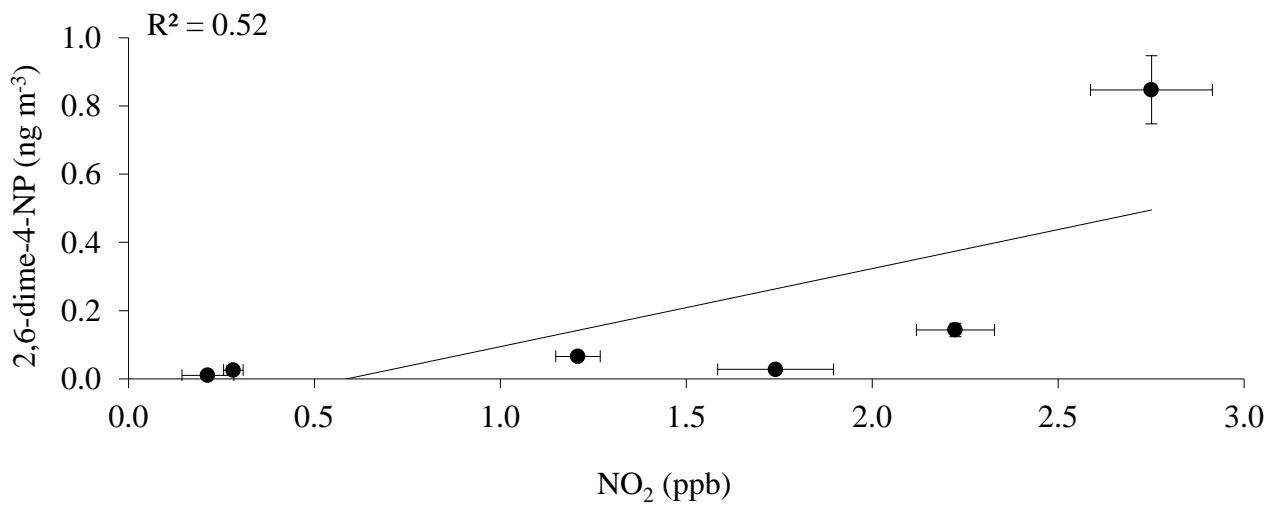
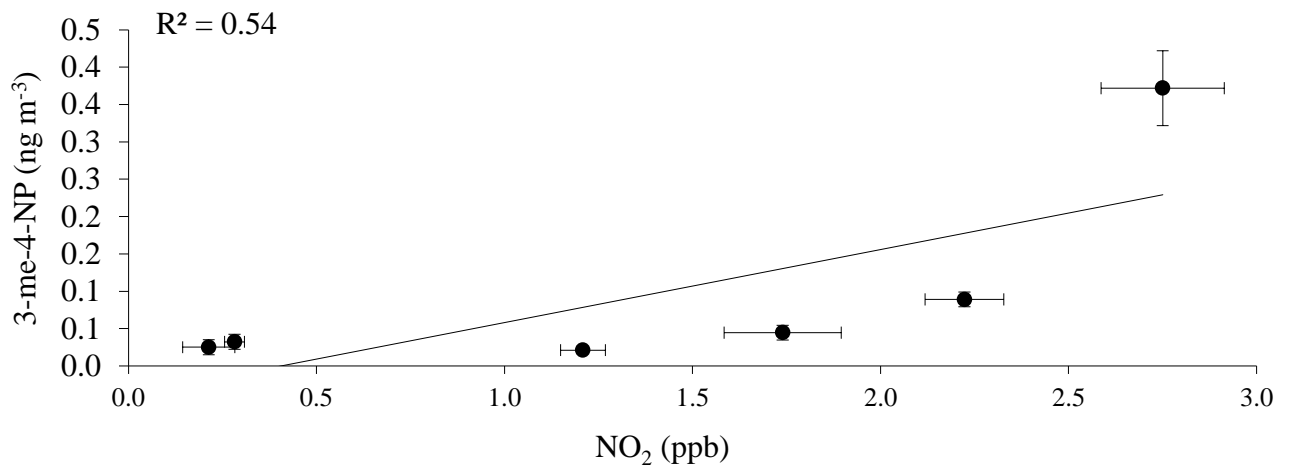
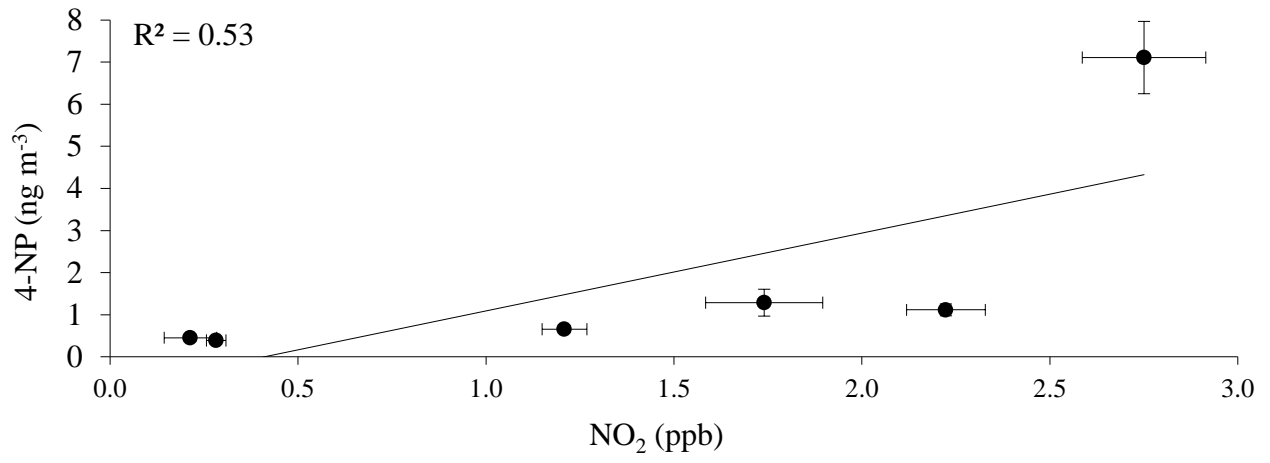
Filter	Average NO ₂ (ppb) ^(a)	Average PM _{2.5} ($\mu\text{g m}^{-3}$) ^(a)	Average O ₃ (ppb) ^(a)
T-X230713A-Top	3.7	4.8	28.0
T-X230713A-Bottom	3.7	4.8	28.0
T-X291013A-Top	25.1	7.9	6.9
T-Q291013B-Bottom	25.1	7.9	6.9
T-X121213A	14.4	10.4	20.1
T-Q121213B	14.4	10.4	20.1
T-X130114C	17.6	10.4	16.5
T-SQ130114C	17.6	10.4	16.5
T-X160215A	31.6	13.4	12.5
T-Q160215B	31.6	13.4	12.5
T-X230215A	15.7	9.6	23.0
T-Q230215B	15.7	9.6	23.0

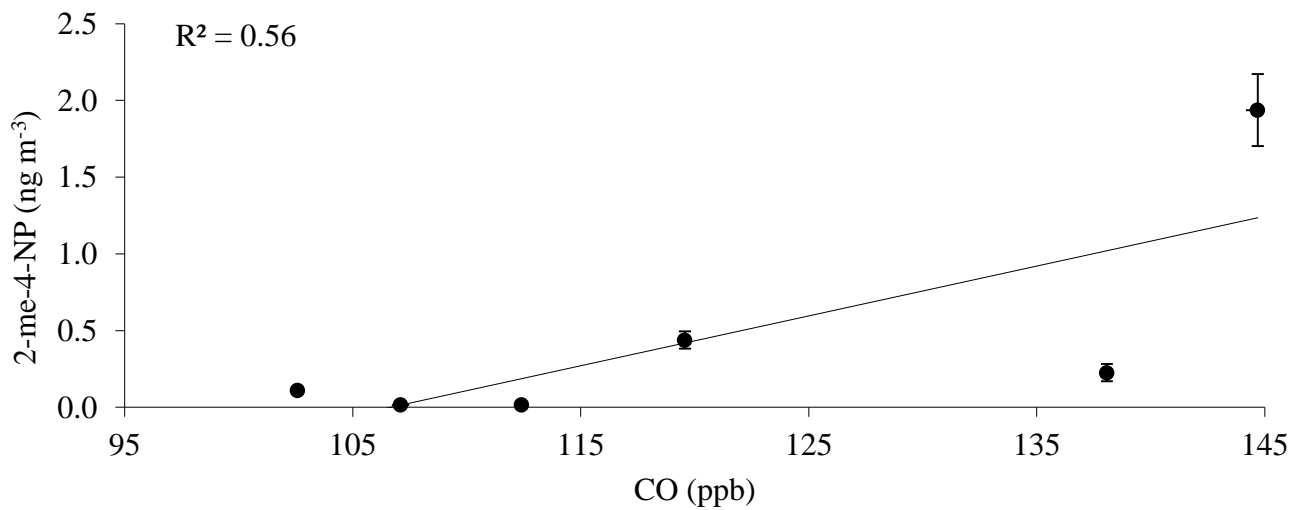
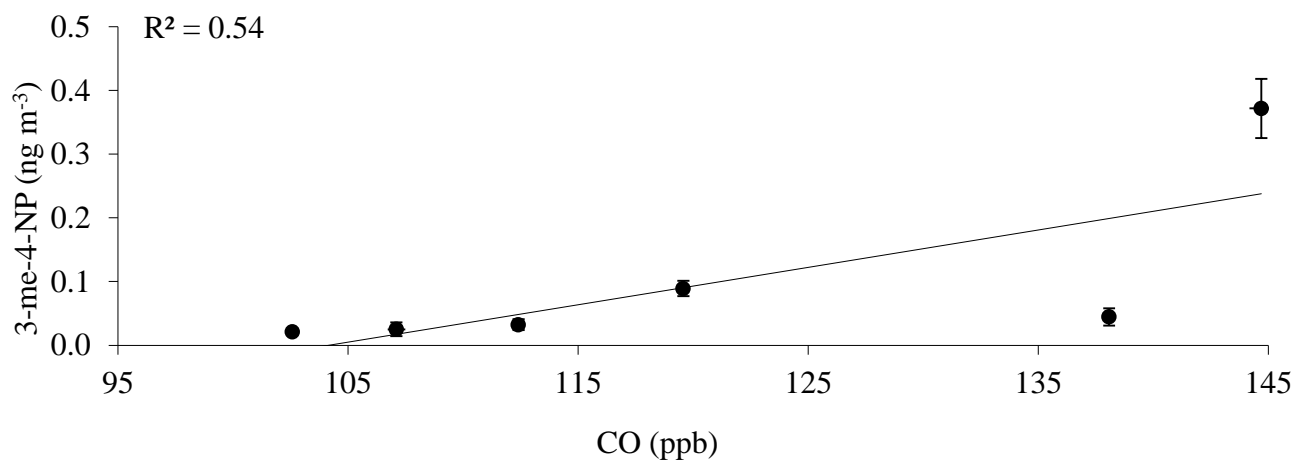
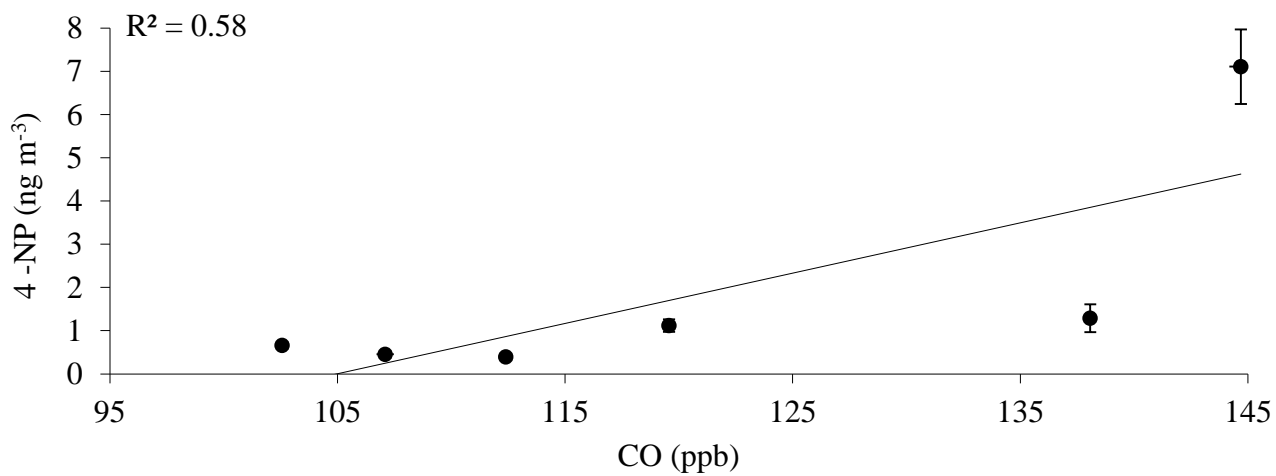
^a Pollution data are averaged over the sampling time and obtained from Ontario Ministry of the Environment: Historical Pollutant, data, Toronto North Site.

Appendix D: Nitrophenol correlation with SO₂, NO₂ and CO. Oil Sands samples.

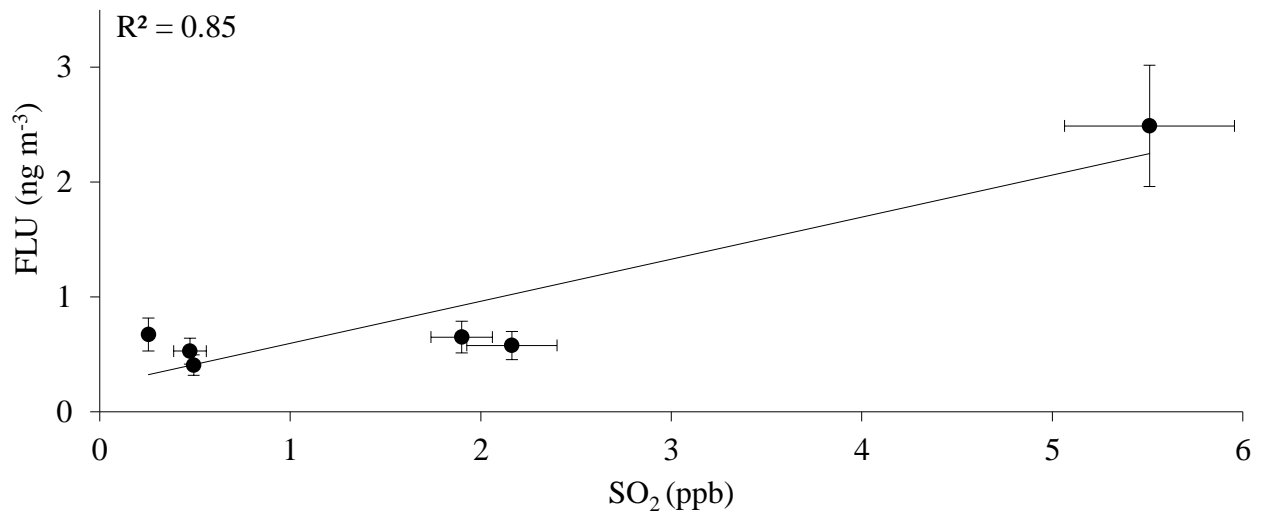
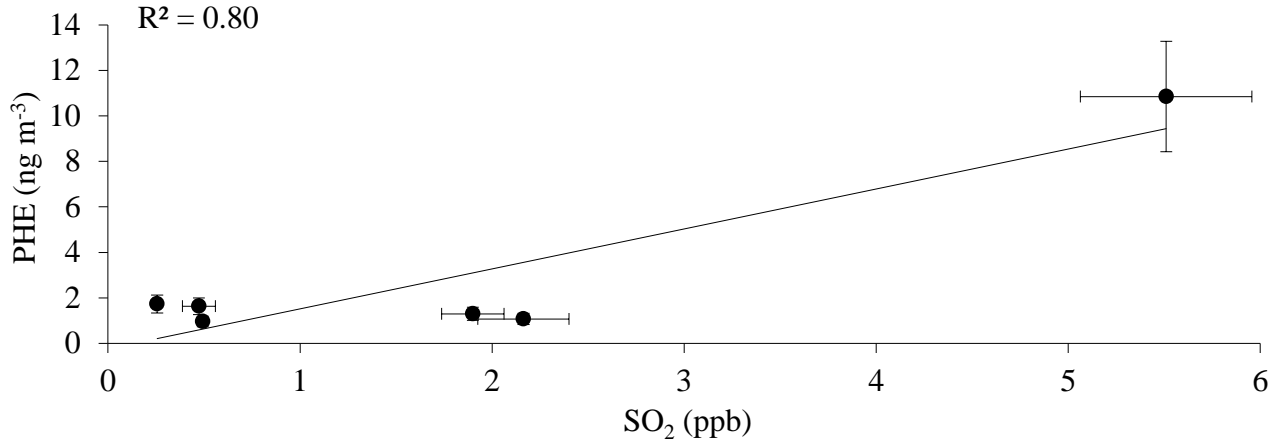
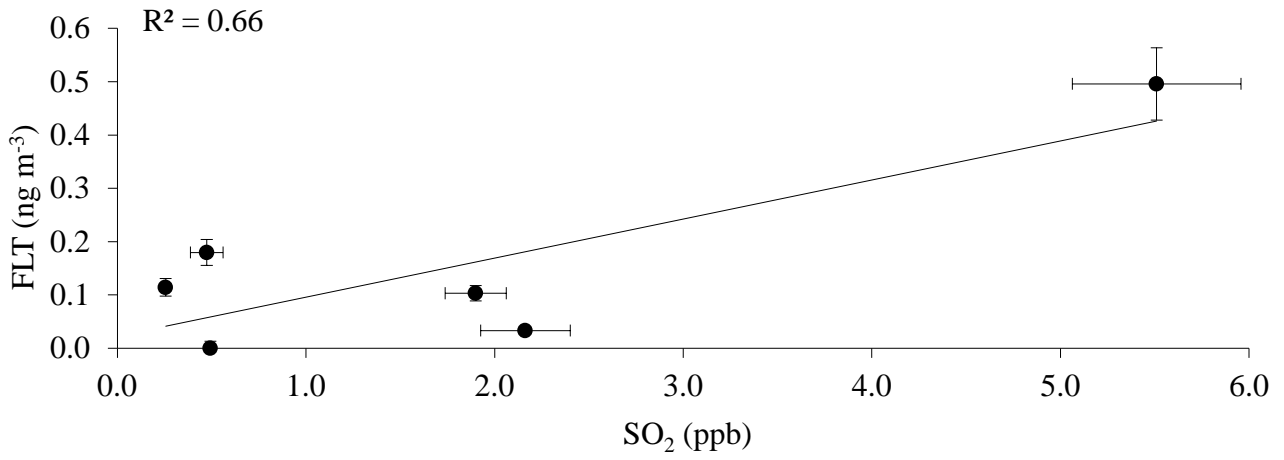


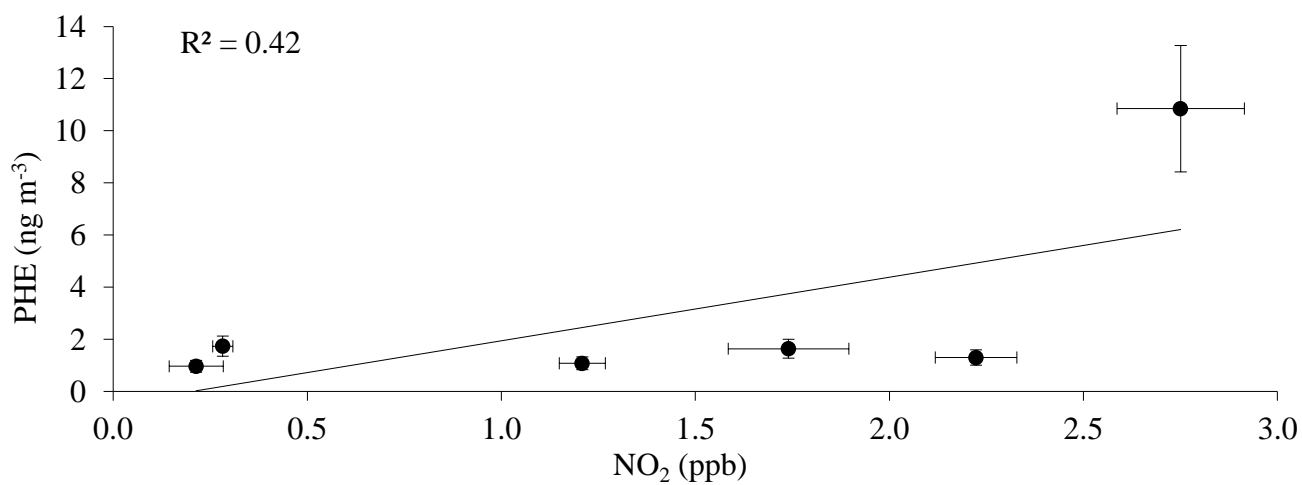
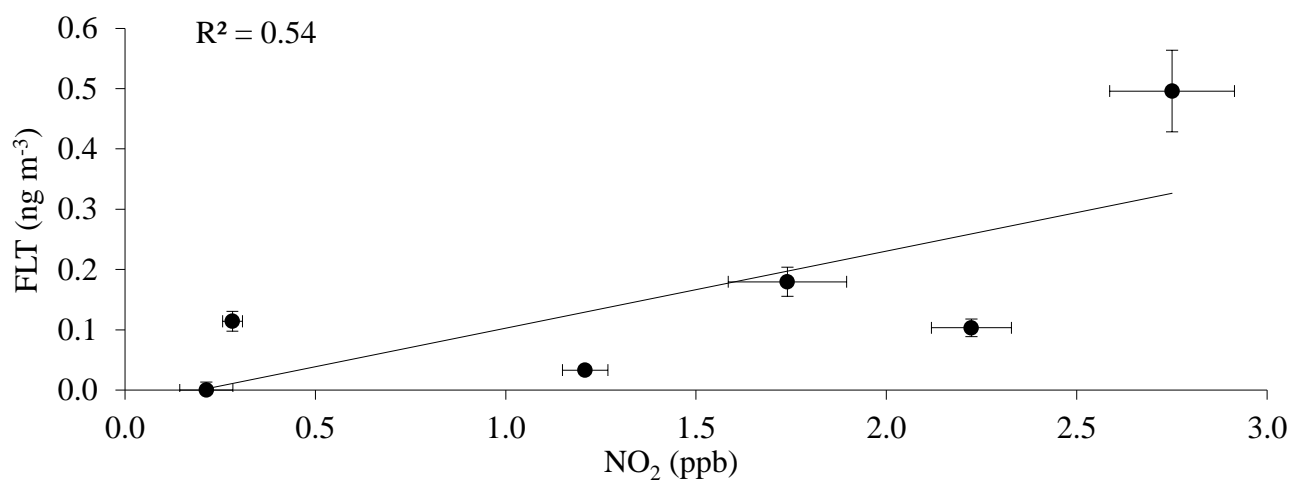
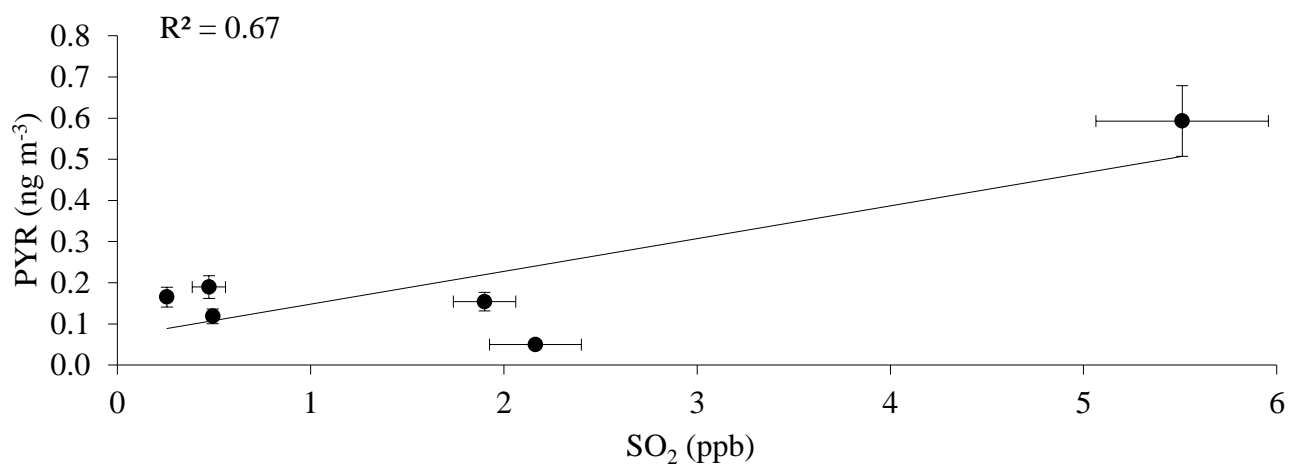


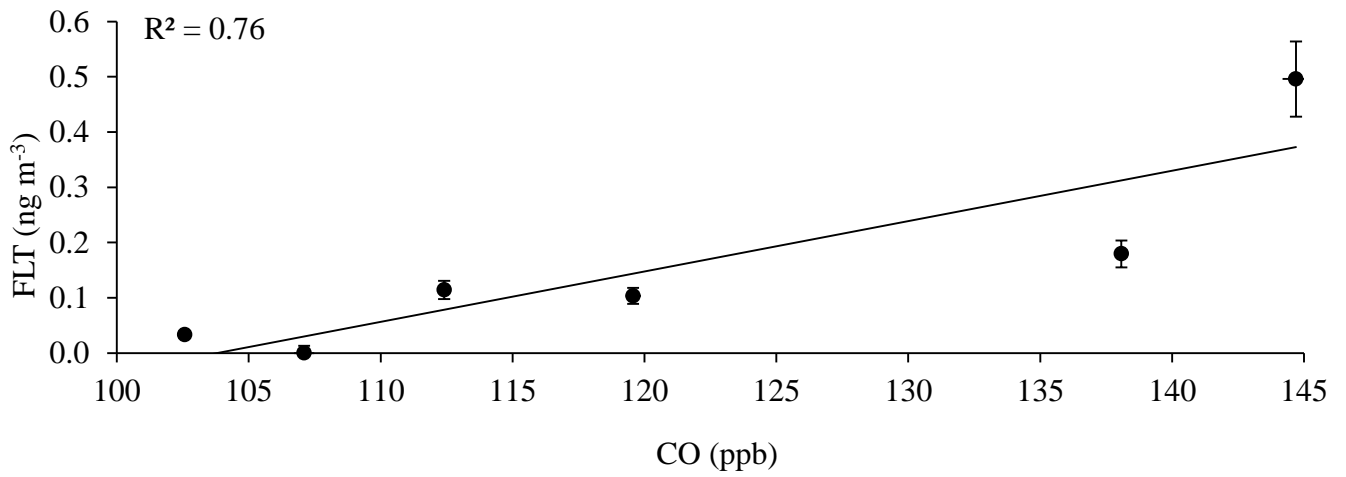
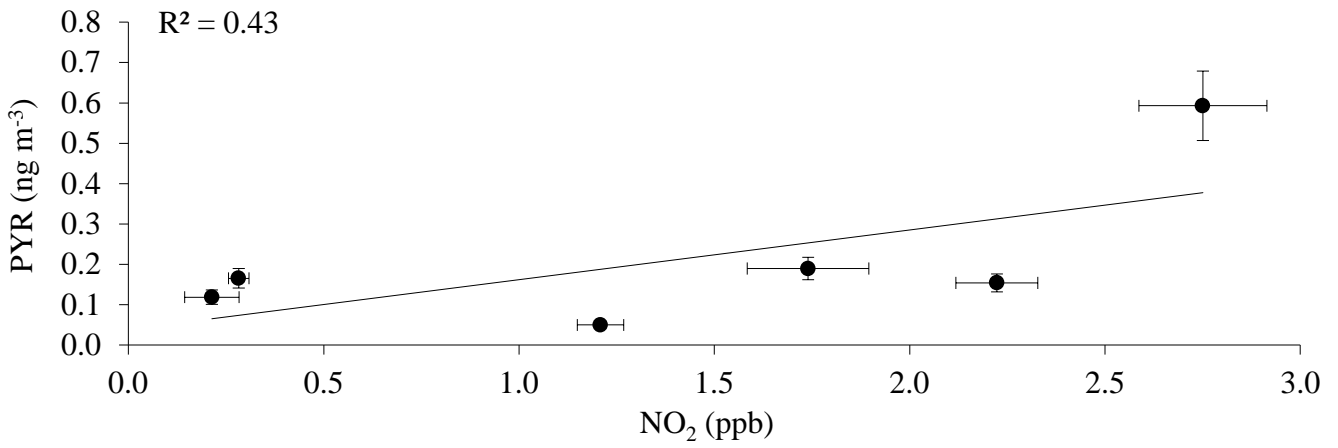
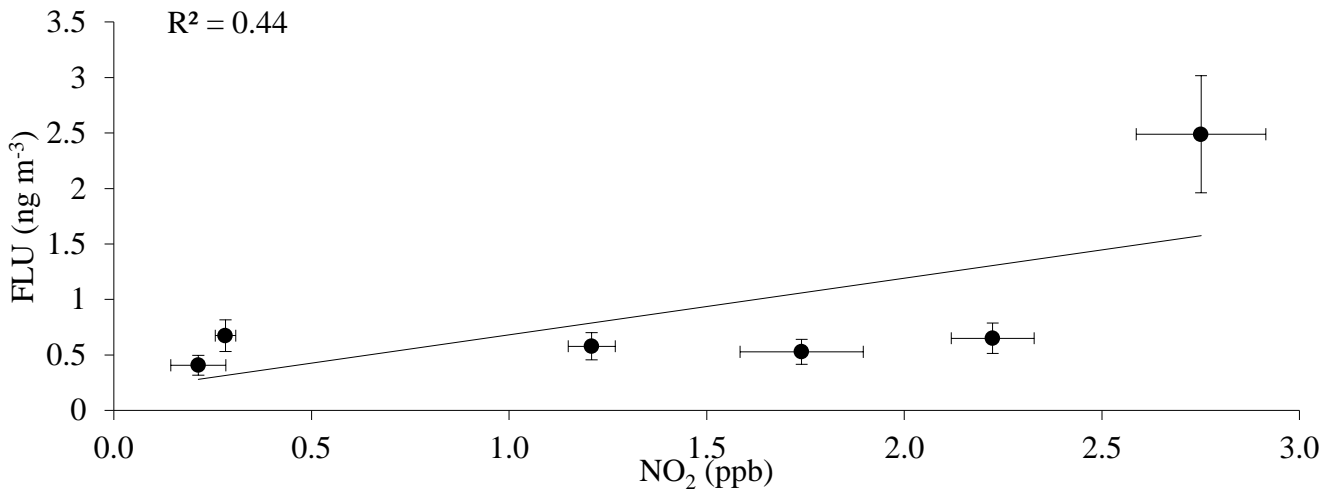


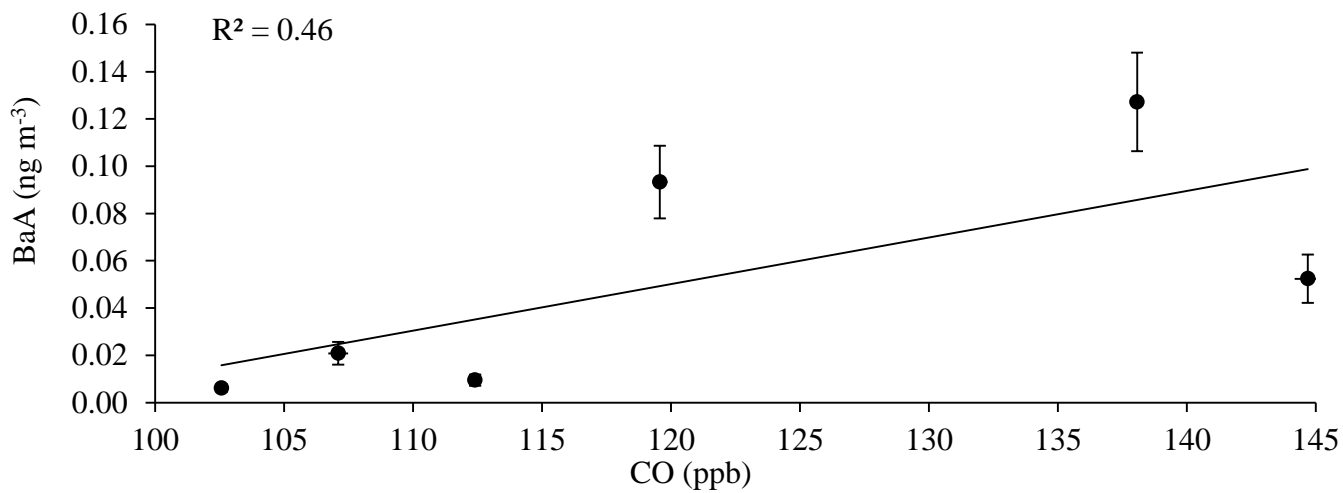
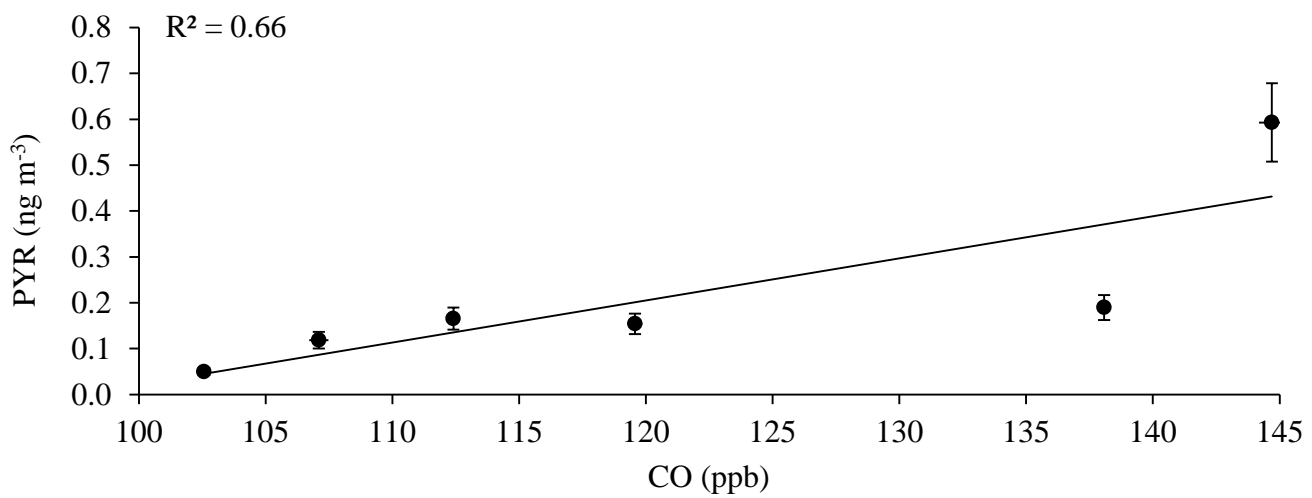
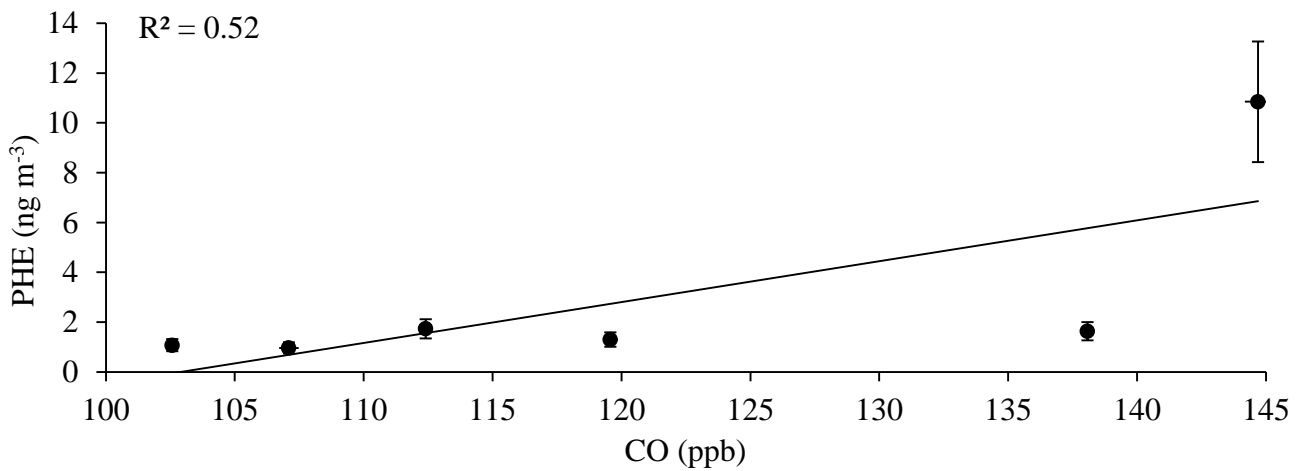


Appendix E: PAH correlation with SO₂, NO₂, CO and CH₄. Oil Sands samples.

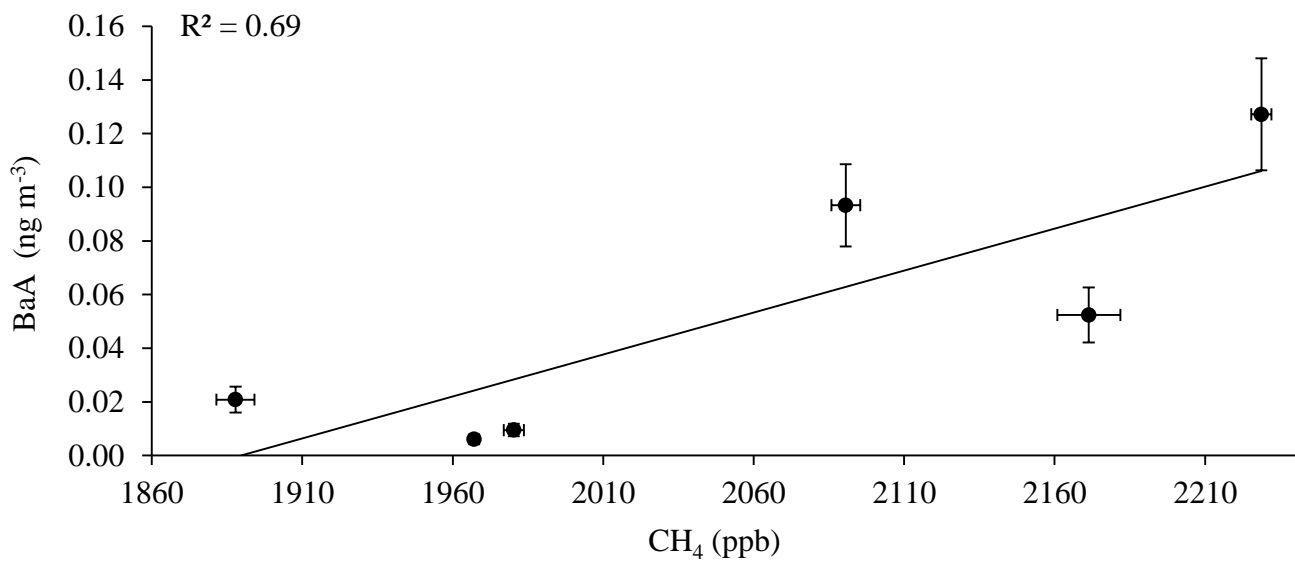
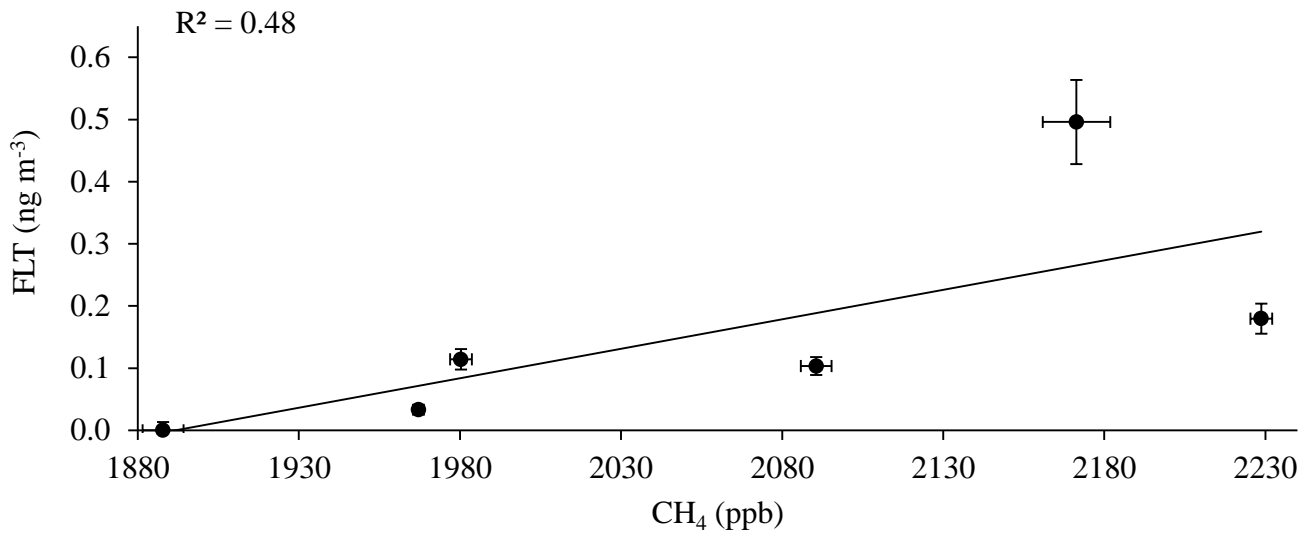








X



Appendix F: n-Alkane correlation with SO₂ and NO₂. Oil Sands samples.

